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(54) **Title:** AN ELECTROLYZER POROUS DIAPHRAGM, METHOD FOR PRODUCING THE SAME, AN ELECTROLYZER COMPRISING THE POROUS DIAPHRAGM, AND USE OF THE POROUS DIAPHRAGM IN ELECTROLYSIS

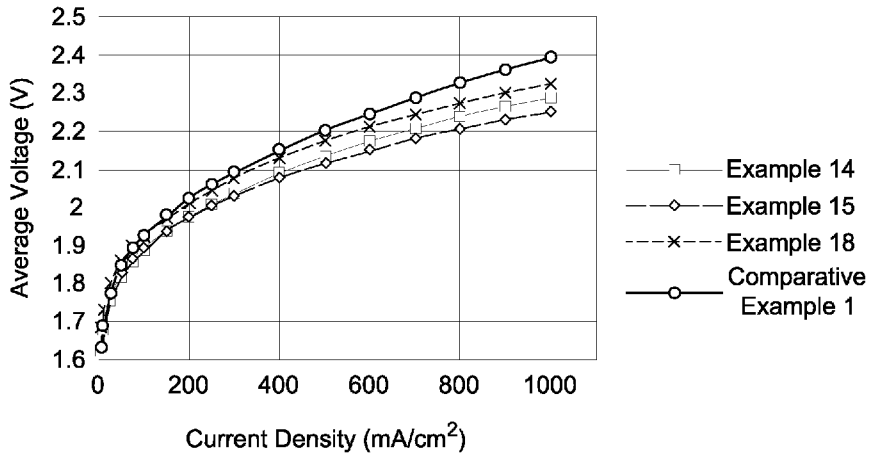


Fig. 1

(57) **Abstract:** The present disclosure provides an electrolyzer porous diaphragm comprising: a microporous polymer scaffold having a plurality of pores having inner surfaces, wherein the microporous polymer scaffold has a first direction, a second direction and a thickness direction, wherein the first direction is orthogonal to the second direction, and the first and second directions are each orthogonal to the thickness direction; and a hydrophilic additive, wherein the hydrophilic additive is deposited on the inner surfaces of the plurality of pores of the microporous polymer scaffold, wherein the microporous polymer scaffold has a matrix tensile strength (MTS) in the second direction of at least about 55 MPa, wherein the second direction is the direction in which the microporous polymer scaffold has its minimum matrix tensile strength, and wherein the porous diaphragm has a contact thickness of less than about 150 μm. The present disclosure also provides a method for producing the electrolyzer porous diaphragm, an electrolyzer comprising the electrolyzer porous diaphragm, and use of the electrolyzer porous diaphragm or the electrolyzer in the electrolysis of water to produce

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AN ELECTROLYZER POROUS DIAPHRAGM, METHOD FOR PRODUCING THE SAME, AN ELECTROLYZER COMPRISING THE POROUS DIAPHRAGM, AND USE OF THE POROUS DIAPHRAGM IN ELECTROLYSIS

FIELD OF INVENTION

[0001] The present disclosure relates to an electrolyzer porous diaphragm, which may find use as e.g., an electrolyzer porous diaphragm for liquid alkaline water electrolysis. The present disclosure also relates to a method for producing the electrolyzer porous diaphragm, an electrolyzer comprising the electrolyzer porous diaphragm, and use of the electrolyzer porous diaphragm or the electrolyzer in the electrolysis of water to produce hydrogen, especially "Green" hydrogen with a low CO_2 footprint.

BACKGROUND

[0002] Porous diaphragms find many uses. One use is in liquid alkaline water electrolysis, which is an important technology for the production of hydrogen. During liquid alkaline water electrolysis, electricity is employed to decompose water into oxygen and hydrogen gas. The hydrogen gas produced is an energy carrier and may be compressed, stored, and used, for example, in a hydrogen fuel cell to generate electricity. The oxygen produced may be either released into the atmosphere or used for a variety of purposes in industry or, for example, as a medical gas.

[0003] An electrolyzer is an electrochemical device in which electrolysis may occur. The liquid alkaline water electrolyzer comprises an anode, a cathode, an electrolyzer porous diaphragm positioned between the anode and the cathode, and a liquid alkaline electrolyte. The electrolyzer porous diaphragm should be non-conductive to electrons to avoid electrical shorts between the electrodes. However, the electrolyzer porous diaphragm should allow hydroxide ions to migrate through, while separating product gases (e.g., hydrogen and oxygen). During liquid alkaline water electrolysis, the half reaction occurring at the anode is: $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$, and the half reaction occurring at the cathode is: $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$. The hydroxide ions migrate from the cathode to the anode through the electrolyzer porous diaphragm.

[0004] Dramatic market growth for large-scale liquid alkaline water electrolysis is expected in the near future as the world ramps up production of hydrogen. The expected increase in global capacity for liquid alkaline water electrolysis, and the intermittent nature of renewable energy that may power the electrolyzers, is driving the need for improvements in liquid alkaline water electrolysis technology, including improved electrolyzer porous diaphragms.

[0005] The main problem with current state-of-the-art electrolyzer porous diaphragms is that they have high ionic resistance due to their large thicknesses, which range from approximately 200-1000 μm. While a large thickness is detrimental to ionic resistance and thus the overall performance of the electrolyzer porous diaphragm, a large thickness enhances the ability of the electrolyzer porous diaphragm to perform other important functions such as reducing gas crossover; preventing electrical shorting; and enabling robust shipping, storage, and handling to enable large-scale electrolyzer assembly (herein referred to as "handleability"). Reducing gas crossover is important because, for example, if enough hydrogen crosses over into the oxygen stream, an explosion may occur. The explosive limit is approximately 4 mol% hydrogen in oxygen and most electrolyzers are designed to keep the hydrogen concentration below a fraction of the explosive limit, for example below 2 mol% or below 1 mol%. Electrical shorting must be prevented because, for example, it may result in loss of efficiency or in an unsafe operating condition. Good handleability is important to enable the industry to scale up to Gigawatt volumes economically.

[0006] Thus, there is a need for electrolyzer porous diaphragms which e.g., may be used in liquid alkaline water electrolysis and have reduced ionic resistance, while maintaining adequately low gas crossover, preventing electrical shorting, and having good handleability.

[0007] Moreover, there is a need for electrolyzer porous diaphragms for liquid alkaline water electrolysis which may function effectively at higher operating temperatures than the current state-of-the-art electrolyzer porous diaphragms. Currently, about 90°C is generally considered the maximum operating temperature for a liquid alkaline water electrolyzer comprising a state-of-the-art electrolyzer porous diaphragm, and there is a need for diaphragms which allow for higher operating temperatures and thus improved efficiency (for example, because higher operating temperatures may reduce the ionic resistance of the electrolyte in the electrolyzer porous diaphragm and increase the activity of the electrodes).

[0008] There is also a need for electrolyzer porous diaphragms for liquid alkaline water electrolysis which enable storage and installation of the diaphragm in the electrolyzer in a dry state, contributing to improved handleability and high-volume manufacturing.

SUMMARY

[0009] The present disclosure addresses the problems and needs described above.

[00010] In a first aspect, there is provided an electrolyzer porous diaphragm comprising: a microporous polymer scaffold having a plurality of pores having inner surfaces, wherein the microporous polymer scaffold has a first direction, a second direction and a thickness direction, wherein the first direction is orthogonal to the second direction, and the first and second

directions are each orthogonal to the thickness direction; and a hydrophilic additive, wherein the hydrophilic additive is deposited on the inner surfaces of the plurality of pores of the microporous polymer scaffold, wherein the microporous polymer scaffold has a matrix tensile strength (MTS) in the second direction of at least about 55 MPa, wherein the second direction is the direction in which the microporous polymer scaffold has its minimum matrix tensile strength, and wherein the electrolyzer porous diaphragm has a contact thickness of less than about 150 μm.

[00011] It has been surprisingly discovered by the inventors that the electrolyzer porous diaphragm, which has a contact thickness of less than about 150 μm and comprises a microporous polymer scaffold having a matrix tensile strength (MTS) in the second direction of at least about 55 MPa, enables an ideal balance of properties for use as an electrolyzer porous diaphragm, e.g. in liquid alkaline water electrolysis. Specifically, the electrolyzer porous diaphragm has low ionic resistance due to the thickness of the diaphragm, while also having low gas crossover, excellent handleability and excellent electrical shorting resistance. The microporous polymer scaffold having a matrix tensile strength (MTS) in the second direction of at least about 55 MPa contributes to the microporous polymer scaffold having excellent strength properties, which aid the handleability and resistance to electrical shorting. The microporous polymer scaffold having a matrix tensile strength (MTS) in the second direction of at least about 55 MPa also allows the electrolyzer porous diaphragm to be thin, i.e., less than about 150 μm, which improves the ionic resistance relative to an otherwise identical but thicker diaphragm.

[00012] Compared to the current state-of-the-art electrolyzer porous diaphragms for liquid alkaline water electrolysis, the electrolyzer porous diaphragm according to the present disclosure having the above-described properties enables an improved balance of properties (low ionic resistance, low gas crossover, excellent handleability and excellent electrical shorting resistance) for use as an electrolyzer porous diaphragm in liquid alkaline water electrolysis. One reason for this is that the current state-of-the-art electrolyzer porous diaphragms are typically thicker (ranging from approximately 200-1000 μm) than the electrolyzer porous diaphragms according to the present disclosure, and therefore generally have higher ionic resistance.

[00013] The electrolyzer porous diaphragms of the present disclosure enable storage and installation of the diaphragm in the electrolyzer in a dry state, contributing to improved handleability and high-volume manufacturing over current state-of-the-art electrolyzer porous diaphragms which may require wet state installation. This is because microporous scaffolds may

secure/hold the hydrophilic additive without the need for additional binder, thereby improving the stability of the electrolyzer porous diaphragm in the dry-state relative to diaphragms using binders to bond particles to a microporous support.

[00014] The hydrophilic additive ensures sufficient non-dewettability of the electrolyzer porous diaphragm. In liquid alkaline water electrolysis, the electrolyzer porous diaphragm needs to get wet with electrolyte and stay wet, preferably totally, for low ionic resistance. Without being bound by theory, it is believed it is critical for the electrolyte porous diaphragm to be hydrophilic to prevent bubbles from the electrolyte from nucleating on and/or sticking to and therefore "blinding" the diaphragm by de-wetting, thus increasing its ionic resistance.

[00015] In one embodiment, the microporous polymer scaffold may have a geometric mean MTS of at least about 90 MPa. The geometric mean MTS refers to the square root of the product of the MTS in the first direction and the MTS in the second direction. The microporous polymer scaffold having a geometric mean MTS of at least about 90 MPa results in excellent strength properties of the electrolyzer porous diaphragm.

[00016] In one embodiment, the geometric mean absolute tensile strength of the microporous polymer scaffold / electrolyzer porous diaphragm contact thickness may be at least about 10 MPa.

[00017] In one embodiment, the absolute tensile strength of the microporous polymer scaffold in the second direction / electrolyzer diaphragm contact thickness may be at least about 8 MPa.

[00018] In one embodiment, the microporous polymer scaffold may have a tensile strength balance ratio (absolute tensile strength in the second direction / absolute tensile strength in the first direction) in the range of from 0.45 and 1. Given that the absolute tensile strength in the second direction is less than (or equal to) the absolute tensile strength in the first direction, a tensile balance of 1 is perfectly balanced, i.e., the absolute tensile strengths in the first and second directions are the same. Generally, values closer to 1 are more desirable than smaller values because the strength of the scaffold varies less in each direction and is therefore more uniform. This is desirable assuming that the mechanical stresses during production, shipping, handling, storage, installation and use will be applied to the electrolyzer porous diaphragm more or less uniformly, i.e., they will not be preferentially applied in one particular direction.

[00019] In one embodiment, the microporous polymer scaffold may have a mass-per-area ranging from about 1 g/m^2 to about 60 g/m^2. If the mass-per-area is too high, the ionic resistance of the electrolyzer porous diaphragm may be too high, and it may become difficult to deposit a uniform coating of the hydrophilic additive over the microporous polymer scaffold. If the

mass-per-area is too low, the handleability, gas crossover and resistance to electrical shorting may suffer.

[00020] In one embodiment, the microporous polymer scaffold may have a porosity of at least about 40 vol% or of at least about 75 vol%. If the porosity is too low, it may be difficult to deposit a uniform coating of the hydrophilic additive over the microporous polymer scaffold. At very low porosities, the ionic conductance of the resulting electrolyzer porous diaphragm may be too low.

[00021] In one embodiment, the electrolyzer porous diaphragm may have a contact thickness ranging from about 2 μm to about 75 μm. If the electrolyzer porous diaphragm is too thick, the ionic resistance may be too high. Generally, the thinner the electrolyzer porous diaphragm, the lower the ionic resistance. If the electrolyzer porous diaphragm is too thin, handleability, gas crossover and resistance to shorting may suffer.

[00022] In one embodiment, the microporous polymer scaffold may have a bubble point pressure of at least about 1 bar (or about 15 psi). A high bubble point may result in an electrolyzer porous diaphragm with improved handleability and resistance to shorting, while being able to remain thin and therefore maintain low ionic resistance.

[00023] In one embodiment, the electrolyzer porous diaphragm may comprise one or more microporous polymer scaffolds. The one or more microporous polymer scaffolds may be formed from the same polymer or different polymers.

[00024] In one embodiment, the microporous polymer scaffold may be formed from any one selected from a non-fluorinated polymer, a partially fluorinated polymer, a perfluorinated polymer, and any combination thereof. The microporous polymer scaffold may be formed from any one selected from a polytetrafluoroethylene (PTFE), a polyethylene (PE), a polypropylene (PP) or a copolymer thereof, such as a copolymer of PTFE and PE. The microporous polymer scaffold may be formed from expanded PTFE (ePTFE) or expanded PE (ePE). It is important that the microporous polymer scaffold is stable to base, so that when the electrolyzer porous diaphragm is used in alkaline electrolysis, it does not degrade to a significant extent and therefore can function as intended. The above polymers are base stable and therefore suitable for use in alkaline electrolysis.

[00025] In one embodiment, the microporous polymer scaffold may have a microstructure comprising nodes, fibrils, and the plurality of scaffold pores, wherein the nodes are interconnected by the fibrils, and the plurality of scaffold pores are void spaces between the nodes and fibrils.

[00026] In one embodiment, the hydrophilic additive may be deposited on the surfaces of the nodes and fibrils of the microporous polymer scaffold without occluding the scaffold pores. The

microporous polymer scaffold therefore remains porous. If the scaffold pores of the electrolyzer porous diaphragm are occluded when in use in the intended application, the ionic conductance may be impaired.

[00027] In one embodiment, the hydrophilic additive may be deposited on the surfaces of the nodes and fibrils throughout a thickness of the microporous polymer scaffold. This ensures that the hydrophilic additive can perform its function throughout the thickness of the microporous polymer scaffold.

[00028] In one embodiment, the microporous polymer scaffold may have a first surface and a second surface opposite the first surface, and wherein the hydrophilic additive may be deposited on the first surface of the microporous polymer scaffold and/or the second surface of the microporous polymer scaffold.

[00029] In one embodiment, the electrolyzer porous diaphragm may contain from about 2 wt% to about 95 wt% of the hydrophilic additive, wherein the total weight of the porous diaphragm is 100 wt%. If the hydrophilic additive content is too high, the ionic conductance may suffer by e.g., reducing porosity, increasing tortuosity and increasing Donnan exclusion. If the hydrophilic additive content is too low, the non-dewettability of the microporous polymer scaffold may be unsatisfactory, which may increase the ionic resistance of the diaphragm. The electrolyzer porous diaphragm may contain from about 10 wt% to about 95 wt% or from about 25 wt% to about 95 wt% or from about 50 wt% to about 95 wt% of the hydrophilic additive.

[00030] In one embodiment, the hydrophilic additive may comprise a polymer or ceramic. The polymer may be an ionomer (i.e., an ion-exchange polymer) selected from any one of an anion exchange ionomer (e.g., an aminated ionomer), a cation exchange ionomer (e.g., a sulfonated ionomer), and a combination thereof, wherein the ionomer may be perfluorinated (e.g., a perfluorosulfonic acid), partially fluorinated, or non-fluorinated (e.g., hydrocarbon-based). The ionomer may comprise heteroatoms other than fluorine. The ionomer may comprise aromatic moieties and/or non-aromatic (e.g., aliphatic or olefinic) moieties. The polymer may also be non-ionic (e.g., a perfluoropolyether). The hydrophilic additive should have sufficient chemical durability so that degradation of the additive does not cause the diaphragm to fail to function in the intended application. For example, a hydrophilic additive for an electrolyzer porous diaphragm for liquid alkaline water electrolysis must be durable in strong base (e.g., 30 wt% KOH in water) super-saturated with product gases such as oxygen and at the temperatures and time periods required for the application (e.g., about 80°C-90°C for up to about 10,000 hours). In one embodiment, the ionomer may be a perfluorosulfonic acid or a

salt of a perfluorosulfonic acid. In another embodiment, the ceramic may be selected from any one of silica, alumina, titania, ceria, zirconia, yttria-stabilized zirconia, and a combination thereof. The use of ceramic with the microporous polymer scaffold (e.g., ePTFE) without any binder allows for the electrolyzer porous diaphragm to be stable to high heat, typically much higher than the 90-100°C maximum currently used in liquid alkaline water electrolysis.

[00031] In one embodiment, the hydrophilic additive may be deposited on the inner surfaces of the plurality of pores of the microporous polymer scaffold by imbibing the microporous polymer scaffold with an imbibing fluid, wherein the imbibing fluid comprises the hydrophilic additive and a liquid carrier, and drying the microporous polymer scaffold imbibed with the imbibing fluid. The liquid carrier may be any one selected from water, a C1-C5 alcohol and any combination thereof, wherein the C1-C5 alcohol may be any one selected from methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol and pentan-1-ol. In one embodiment, the imbibing fluid may be prepared by dissolving or mixing the hydrophilic additive in the liquid carrier.

[00032] In one embodiment, the hydrophilic additive may be imbibed such that it is substantially contained within the pores of the microporous polymer scaffold (i.e., the thickness of hydrophilic additive deposited on the first or second surface of the microporous polymer scaffold, outside the pore volume of the microporous polymer scaffold, sometimes referred to as “buttercoat” layers, is minimal). The thickness of such a buttercoat layer may be less than 2 microns, or less than 1 micron, or less than 0.5 microns, or less than 0.2 microns, or less than 0.1 microns. Alternatively, one or both of the first and second surfaces of the microporous polymer scaffold may be free from hydrophilic additive layers i.e. there is no layer of hydrophilic additive on one or both of the first and second surfaces of the microporous polymer scaffold e.g. there is no layer of hydrophilic additive which is fee from microporous polymer scaffold.

[00033] In one embodiment, the electrolyzer porous diaphragm may be for liquid alkaline water electrolysis. Other uses of the electrolyzer porous diaphragm may be envisaged, but the electrolyzer porous diaphragm is particularly well-suited for liquid alkaline water electrolysis.

[00034] In one embodiment, the electrolyzer porous diaphragm may further comprise a liquid electrolyte. The liquid electrolyte may be a liquid alkaline electrolyte. The liquid alkaline electrolyte may be an aqueous liquid alkaline electrolyte. The liquid alkaline electrolyte may comprise a strong base. The liquid alkaline electrolyte may comprise sodium hydroxide or potassium hydroxide. The electrolyte may be present in the plurality of pores of the microporous polymer scaffold.

[00035] In one embodiment, the electrolyzer porous diaphragm is provided on a backer. The backer may be selected from a film or fabric, such as a woven material or a non-woven material, such as a web.

[00036] In one embodiment, the electrolyzer porous diaphragm may have a low diaphragm collapse. Diaphragm collapse is an indication of the dimensional stability of the electrolyzer porous diaphragm. The diaphragm collapse may be expresses by the following formula:

[00037] $(diaphragm_{nct}\text{-}diaphragm_{ct})/diaphragm_{nct} \times 100\%$

[00038] wherein $diaphragm_{nct}$ is the non-contact thickness of the electrolyzer porous diaphragm and $diaphragm_{ct}$ is the contact thickness of the electrolyzer porous diaphragm. The diaphragm collapse may be ≤ 25% or may be ≤ 10%, or may be ≤ 5%.

[00039] In one embodiment, the electrolyzer porous diaphragm may have a low gas permeance. The low gas permeance may be represented by a Gurley number ≥ 500 s or a Gurley number ≥ 1000 s or a Gurley number ≥ 2000 s or a Gurley number ≥ 5000 s.

[00040] In one embodiment, the electrolyzer porous diaphragm may have a low liquid permeance. The liquid permeance may be ≤ 100 $L/m^2/h/bar$ or ≤ 50 $L/m^2/h/bar$ or ≤ 10 $L/m^2/h/bar$ at a differential pressure in the range of from 1 to 50 bar and with isopropyl alcohol as the challenge fluid.

[00041] In one embodiment, the electrolyzer porous diaphragm is stable in the liquid alkaline electrolyte. This means that the components e.g. the microporous polymer scaffold and hydrophilic additive, and properties of the electrolyzer porous diaphragm do not degrade to a significant extent in the liquid alkaline electrolyte such that the electrolyzer porous diaphragm can function as intended. This may be evident from the stability of one or more of the properties of the electrolyzer porous diaphragm in the liquid alkaline electrolyte, such as MTS, bubble point or MPA over time, such as over a period of 24 hours, 1 week, 1 month, up to 3 months, up to 6 months, and up to 1 year.

[00042] In a second aspect, there is provided a porous diaphragm comprising: a microporous polymer scaffold having a plurality of pores having inner surfaces; and a hydrophilic additive, wherein the hydrophilic additive is deposited on the inner surfaces of the plurality of pores of the microporous polymer scaffold, wherein the electrolyzer porous diaphragm has a first direction, a second direction and a thickness direction, wherein the first direction is orthogonal to the second direction, and the first and second directions are each orthogonal to the thickness direction, wherein the electrolyzer porous diaphragm has an absolute tensile strength in the second direction / electrolyzer porous diaphragm contact thickness of at least about 8 MPa, wherein the second direction is the direction in which the electrolyzer porous diaphragm has

its minimum absolute tensile strength, and wherein the electrolyzer porous diaphragm has a contact thickness of less than about 150 μm.

[00043] The above-described embodiments and their advantages also apply to the second aspect.

[00044] In a third aspect, there is provided a method of producing an electrolyzer porous diaphragm according to the present disclosure, the method comprising: imbibing the microporous polymer scaffold with an imbibing fluid, wherein the imbibing fluid comprises the hydrophilic additive and a liquid carrier; and drying the microporous polymer scaffold imbibed with the imbibing fluid.

[00045] In one embodiment, the liquid carrier may be any one selected from water, a C1-C5 alcohol and any combination thereof, wherein the C1-C5 alcohol may be any one selected from methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol and pentan-1-ol. In one embodiment, the method may further comprise preparing the imbibing fluid by dissolving or mixing the hydrophilic additive in the liquid carrier.

[00046] In a fourth aspect, there is provided an electrolyzer comprising: an anode; a cathode; the electrolyzer porous diaphragm according to the present disclosure; and a liquid electrolyte, wherein the electrolyzer porous diaphragm is positioned between the anode and the cathode, and wherein the liquid electrolyte at least partially wets the electrolyzer porous diaphragm.

[00047] In one embodiment, the anode and the cathode are gas generating electrodes.

[00048] The anode and cathode (together, the “electrodes”) may comprise any one of the following: nickel, cobalt, iron, platinum, and carbon.

[00049] In one embodiment, the liquid electrolyte is a liquid alkaline electrolyte, optionally wherein the liquid alkaline electrolyte may be an aqueous or substantially aqueous alkaline solution. The liquid alkaline electrolyte may comprise a metal hydroxide. The metal hydroxide may be sodium hydroxide or potassium hydroxide.

[00050] The electrolyzer may be an electrolyzer for liquid alkaline water electrolysis. The electrolyzer porous diaphragm according to the present disclosure is particularly well-suited for liquid alkaline water electrolysis for the reasons discussed herein.

[00051] In a fifth aspect, there is provided a use of the electrolyzer porous diaphragm according to the present disclosure or the electrolyzer according to the present disclosure in the electrolysis of water to produce hydrogen.

[00052] The foregoing embodiments should not be read to limit or otherwise narrow the scope of any of the inventive concepts otherwise provided by the present disclosure. While multiple embodiments are disclosed, other embodiments will become apparent to those skilled in the

art from the following description and drawings. Accordingly, the description and drawings are to be regarded as illustrative rather than restrictive.

BRIEF DESCRIPTION OF THE FIGURES

[00053] Figure 1 shows the polarization curves of current density versus average voltage for the scaffold of Comparative Example 1 and the electrolyzer porous diaphragms of Examples 14, 15 and 18 described herein.

[00054] Figure 2 shows the polarization curves of current density versus average voltage for the scaffold of Comparative Example 1 and the electrolyzer porous diaphragms of Examples 10, 17 and 19 described herein.

[00055] Figure 3 shows the polarization curve slope for the scaffold of Comparative Example 1 and the electrolyzer porous diaphragms of Examples 10, 14, 15, 17, 18 and 19 of the invention.

[00056] Figure 4 shows a schematic representation of a Universal Instron® test system for the determining the force to short of an electrolyzer porous diaphragm.

[00057] The accompanying figures referred to herein are not necessarily drawn to scale but may be exaggerated to illustrate various aspects of the present disclosure, and in that regard, the figures should not be construed as limiting.

DETAILED DESCRIPTION

[00058] The present disclosure relates to an electrolyzer porous diaphragm comprising: a microporous polymer scaffold having a plurality of pores having inner surfaces, wherein the microporous polymer scaffold has a first direction, a second direction and a thickness direction, wherein the first direction is orthogonal to the second direction, and the first and second directions are each orthogonal to the thickness direction; and a hydrophilic additive, wherein the hydrophilic additive is deposited on the inner surfaces of the plurality of pores of the microporous polymer scaffold, wherein the microporous polymer scaffold has a matrix tensile strength (MTS) in the second direction of at least about 55 MPa, wherein the second direction is the direction in which the microporous polymer scaffold has its minimum matrix tensile strength, and wherein the porous diaphragm has a contact thickness of less than about 150 μm.

[00059] As mentioned above, it has been surprisingly discovered by the inventors that such an electrolyzer porous diaphragm has an ideal balance of properties for use as e.g., a diaphragm in liquid water alkaline electrolysis. Specifically, when used in liquid alkaline water electrolysis, the electrolyzer porous diaphragm has low ionic resistance due to the low thickness of the diaphragm, while also having low gas crossover, excellent handleability, and excellent

electrical shorting resistance. Also, the electrolyzer porous diaphragm may enable storage and installation of the diaphragm in an electrolyzer in a dry state, contributing to improved handleability over current state-of-the-art diaphragms which may require installation in a wet state.

[00060] Conventional diaphragms may comprise a woven fabric as a scaffold. Such woven fabrics may have low surface areas, such as a volume specific surface area of about 0.03 $m^2_{surface}/cc$, or an area specific surface area of about 2 $m^2_{surface}/m^2$. Such low surface areas may contribute to such woven fabric scaffolds being relatively easy to wet (e.g., with electrolyte in an electrochemical cell, or with a processing fluid during diaphragm production). The electrolyzer porous diaphragm described herein comprises a microporous polymer scaffold with a matrix tensile strength of at least 55 MPa. Such high matrix tensile strength microporous polymer scaffolds may exhibit a high surface area, such as a volume-specific surface area of at least 0.5 m^2/cc, and particularly at least 10 m^2/cc, or an area-specific surface area of at least 5 $m^2_{surface}/m^2$, and particularly at least 50 $m^2_{surface}/m^2$. Microporous polymer scaffolds with higher specific surface areas are typically difficult to wet, or they may de-wet significantly when exposed to bubbles. However, the electrolyzer porous diaphragms described herein may be wetted with liquid electrolyte and can operate effectively in liquid alkaline water electrolyzers. Surprisingly, in liquid alkaline water electrolysis testing, the electrolyzer porous diaphragms described herein have surpassed the performance of conventional diaphragms with woven fabric scaffold (e.g., as measured by the slope of the polarization curve). In the aforementioned description of surface area, volumetric units (i.e., m^2/cc) were used instead of gravimetric units (i.e., m^2/g) because this disclosure describes scaffolds of a wide variety of polymers with different densities (e.g., hydrocarbons with densities around 1 g/cc and fluoropolymers with densities around 2 g/cc). When designing and analyzing composite materials, the volume fraction of different components is often more meaningful than mass fraction. For example, thickness and porosity, which are inherently volumetric properties, are important considerations to the calculation of ion conductance. As another example, the use of matrix tensile strength (MTS), which is effectively a volume-normalized version of tensile strength, describes the strength of the microporous polymer scaffold. To account for the differences in the skeletal densities of microporous polymer scaffolds, the inventors believe that volume specific surface area is preferable to mass specific surface area. Another potentially useful way to describe surface area is area based, because so many transport and electrochemical parameters are area-based. For example, parameters such as area specific resistance (e.g., expressed in $m\Omega*cm^2$), current density (e.g., expressed

in mA/cm^2), and permeance (e.g., expressed in liters*m^{-2}*h^{-1}*bar^{-1}) are all defined per area. For this reason, surface area was also expressed as the area specific surface area (e.g., expressed in $m^2_{surface}/m^2$). In some fields, area specific surface area is also sometimes referred to as "roughness factor.".

[00061] **[Electrolyzer porous diaphragm]**

[00062] The electrolyzer porous diaphragm comprises at least a microporous polymer scaffold and a hydrophilic additive.

[00063] The electrolyzer porous diaphragm has a contact thickness of less than about 150 μm. The electrolyzer porous diaphragm may have a contact thickness ranging from about 2 μm to about 140 μm, or from about 2 μm to about 130 μm, or from about 2 μm to about 120 μm, or from about 2 μm to about 110 μm, or from about 2 μm to about 100 μm, or from about 2 μm to about 90 μm, or from about 2 μm to about 85 μm, or from about 2 μm to about 80 μm, or from about 2 μm to about 75 μm, or from about 3 μm to about 75 μm, or from about 4 μm to about 75 μm, or from about 5 μm to about 75 μm, or from about 5 μm to about 70 μm, or from about 5 μm to about 65 μm, or from about 5 μm to about 60 μm, or from about 5 μm to about 55 μm, or from about 10 μm to about 55 μm, or from about 10 μm to about 50 μm, or from about 10 μm to about 45 μm, or from about 10 μm to about 40 μm. In the present disclosure, μm has its usual meaning, i.e., μm refers to micrometres or microns. Generally, the thinner the electrolyzer porous diaphragm, the lower the ionic resistance when used in alkaline water electrolysis. However, if the electrolyzer porous diaphragm is too thin, it may lack the durability and barrier properties required to function effectively.

[00064] The contact thickness of the electrolyzer porous diaphragm is measured as indicated in the test methods described herein. The thickness direction of the electrolyzer porous diaphragm is the same as the thickness direction of the microporous polymer scaffold.

[00065] The electrolyzer porous diaphragm may comprise one or more microporous polymer scaffolds. The one or more microporous polymer scaffolds may be formed from the same polymer or different polymers. The number of microporous polymer scaffolds is not particularly limited, and the electrolyzer porous diaphragm may comprise one microporous polymer scaffold, or two microporous polymer scaffolds, or three microporous polymer scaffolds, or four microporous polymer scaffolds, or between 1 and 20 microporous polymer scaffolds, or between 1 and 10 microporous polymer scaffolds.

[00066] The electrolyzer porous diaphragm may comprise other layers and components besides the microporous polymer scaffold and the hydrophilic additive, such that the electrolyzer porous diaphragm is suitable for its intended function.

[00067] In one embodiment, the electrolyzer porous diaphragm may have an absolute tensile strength in the second direction / electrolyzer porous diaphragm contact thickness of at least about 8 MPa, wherein the second direction is the direction in which the electrolyzer porous diaphragm has its minimum absolute tensile strength. The electrolyzer porous diaphragm may have an absolute tensile strength in the second direction / electrolyzer porous diaphragm contact thickness of at least about 10 MPa, or at least about 15 MPa, or at least about 20 MPa, or at least about 30 MPa, or at least about 40 MPa, or at least about 50 MPa. The absolute tensile strength of the electrolyzer porous diaphragm in the second direction / electrolyzer porous diaphragm contact thickness may be from about 10 MPa to about 200 MPa, or from about 15 MPa to about 200 MPa, or from about 20 MPa to about 200 MPa, or from about 30 MPa to about 200 MPa, or from about 40 MPa to about 175 MPa, or from about 50 MPa to about 175 MPa.

[00068] The electrolyzer porous diaphragm may have a bubble point pressure of at least about 1 bar, or at least about 2 bar, or at least about 3 bar, or at least 4 about bar, or at least about 5 bar, or at least about 10 bar, or at least about 15 bar, or at least about 20 bar, or at least about 25 bar, or at least about 30 bar. A high bubble point of the electrolyzer porous diaphragm is desirable to prevent the product gasses from passing through the electrolyzer porous diaphragm. Oxygen permeation reduces hydrogen gas purity and can create explosive mixtures in the hydrogen stream at low oxygen concentrations, and hydrogen permeation reduces oxygen gas purity and can generate explosive gas mixtures in the oxygen stream at low hydrogen concentrations. For alkaline water electrolyzers operating at atmospheric pressures, a bubble point of the electrolyzer porous diaphragm of at least 1 bar (or about 15 psi) is typically required for adequately minimizing gas crossover. However, electrolyzer porous diaphragms with higher bubble point may be desired to ensure safe, robust operation and for alkaline water electrolyzers, for example those operating at elevated pressure.

[00069] The electrolyzer porous diaphragm may have a porosity of at least about 30 vol%. The electrolyzer porous diaphragm may have a porosity in the range of from 30 vol% to 80 vol%.

[00070] **[Microporous polymer scaffold]**

[00071] As used herein, the term “microporous polymer scaffold” refers to a thin, flexible, freestanding, porous polymer structure that may be configured in a variety of forms such as a web (i.e., a long, thin, flexible material typically supplied in roll form), a sheet (e.g., a flat sheet), or a tube (e.g., a round tube). The microporous polymer scaffold may preferably be in the form of a web or flat sheet. As used herein, the term “porous” refers to a structure comprising voids (i.e., pores) and a solid matrix. The pores each have a pore volume, and the plurality of

pores define the total pore volume of the microporous polymer scaffold (i.e., the scaffold pore volume). The solid matrix (i.e., the scaffold matrix) refers to the solid portion of the microporous polymer scaffold, excluding its pore volume.

[00072] The microporous polymer scaffold may have a first major exterior surface (i.e., a first surface) and a second major exterior surface (i.e., a second surface), which is opposite the first surface (in the case of a tube these two surfaces correspond to the inner and outer diameters of the tube). The microporous polymer scaffold may have a thickness, which is the distance between the two major exterior surfaces. The plurality of pores have inner surfaces defined by their interfaces with the scaffold matrix. The inner surface of a pore refers to the surface of the pore which is not on an exterior surface of the scaffold.

[00073] As used herein, the term "microporous" refers to a structure comprising pores that are not visible to the naked eye. The scaffold pores may have an average or median pore size from about 0.01 to 100 μm, e.g., from about 0.01 to 1 μm, or about 0.02 to 25 μm, or about 0.01 to about 10 μm, or about 0.05 to 20 μm, or about 0.1 to 80 μm, or about 0.1 to 50 μm, or about 0.1 to 30μm, or about 0.2 to about 60 μm, or about 0.5 to 50 μm, or any intermediate range or value between about 0.01 to 100 μm.

[00074] The term "microporous" is also used to denote a continuous layer of material comprising pores that create passageways extending from the first surface to the second surface (i.e., from one exterior surface of the layer to the opposite exterior surface of the layer). Such passageways may be described as "through pores." The scaffold pore volume may also comprise pores that are not "through pores" (i.e., some pores may not be connected to both exterior surfaces through the scaffold pore volume). Such pores that are connected to only one exterior surface may be described as "dead-end pores," and such pores that are not connected to either exterior surface may be described as "closed-cell pores." Within the scaffold pore volume, all of the pores may be interconnected and may form a continuous porous network, or all of the pores may be isolated from each other, or there may be any intermediate level of interconnection among the pores.

[00075] The scaffold matrix may comprise a continuous network of interconnected material elements, and the scaffold pores may be void spaces between these material elements. The material elements may comprise a wide variety of structural components that form the building blocks of the overall polymer structure. The material elements are not particularly limited, and may comprise, for example, fibers, bundles of fibers, nodes, and fibrils. In one embodiment, the microporous polymer scaffold may have a microstructure comprising fibers, bundles of fibers, and a plurality of scaffold pores, wherein the fibers and bundles of fibers are interconnected,

and the plurality of scaffold pores are void spaces between the fibers and bundles of fibers. In another embodiment, the microporous polymer scaffold may have a microstructure comprising nodes, fibrils, and a plurality of scaffold pores, wherein the nodes are interconnected by the fibrils, and the plurality of scaffold pores are void spaces between the nodes and fibrils.

[00076] A suitable microporous polymer scaffold depends largely on the intended application. The microporous polymer scaffold may support and mechanically reinforce a composite material (e.g., an electrolyzer porous diaphragm), improving its structural integrity and durability. The microporous polymer scaffold may enable the electrolyzer porous diaphragm to be thin and/or of large area while retaining handleability and other desirable properties. The microporous polymer scaffold preferably has good mechanical properties, and is thermally, chemically, and electrochemically stable in the environment in which the composite material is to be used. The microporous polymer scaffold is also preferably tolerant of any manufacturing steps required in the production of the composite material, and in the subsequent storage, shipping, and handling of the composite material.

[00077] For liquid alkaline water electrolysis, the microporous polymer scaffold should have sufficient chemical durability so that its degradation does not cause the electrolyzer porous diaphragm to fail to function in the intended application. For example, a microporous polymer scaffold for an electrolyzer porous diaphragm for liquid alkaline water electrolysis must be durable in strong base (e.g., 30 wt% KOH in water) super-saturated with product gases such as oxygen and at the temperatures and time periods required for the application (e.g., about 80°C-90°C for up to about 10,000 hours).

[00078] The microporous polymer scaffold may be formed from any suitable material for the intended application. The material is not particularly limited and any material known in the art may be used to form the microporous polymer scaffold. For example, the microporous polymer scaffold may comprise polymeric materials. The polymeric materials may comprise a polymer or a mixture of polymers. The polymeric materials may comprise a homopolymer or a copolymer. The polymeric materials may comprise inorganic polymeric materials and/or organic polymeric materials. The polymeric materials may comprise fluorine and/or other heteroatoms. The polymeric materials may comprise aromatic moieties and/or non-aromatic (e.g., aliphatic or olefinic) moieties. The polymeric materials may comprise side chains and/or functional groups. The polymeric materials may comprise a polymer that is fibrillatable (e.g., PTFE). In one embodiment, the microporous polymer scaffold may be formed from any one selected from a non-fluorinated polymer, a partially fluorinated polymer, a perfluorinated

polymer, and any combination thereof. In one embodiment the microporous polymer scaffold may comprise polyolefins such as polyethylene (PE) or polypropylene (PP). In further embodiments the microporous polymer scaffold may comprise any one selected from a polytetrafluoroethylene (PTFE), a polyethylene (PE), or a copolymer of PTFE and PE. In further embodiments, the microporous polymer scaffold may comprise an expanded polytetrafluoroethylene (ePTFE) or an expanded polyethylene (ePE).

[00079] The polymer forming the microporous polymer scaffold may be expanded by any means known in the art. The microporous polymer scaffold may therefore be formed from any one selected from expanded polytetrafluoroethylene (ePTFE), and expanded polyethylene (ePE).

[00080] In one embodiment, the microporous polymer scaffold may be formed from expanded polytetrafluoroethylene (ePTFE) or expanded polyethylene (ePE). It is important that the microporous polymer scaffold is stable to base, so that when the porous diaphragm is used in alkaline electrolysis, it does not degrade to a significant extent and therefore can function as intended. The above polymers are base stable and therefore suitable for use in alkaline electrolysis.

[00081] The microporous polymer scaffold may be a microporous polymer membrane or a polymer non-woven.

[00082] The microporous polymer scaffold may be formed by any suitable method for the intended application. The method of manufacturing the microporous polymer scaffold is not particularly limited, and any method known in the art may be used to form the microporous polymer scaffold, including processing techniques known in the art for producing membranes and non-wovens. Preferred processing methods may comprise roll-to-roll processing. Preferred processing methods may include paste processing, gel processing, and expansion. Depending largely on the method of manufacture, the microporous polymer scaffold may have a machine direction (MD) and a transverse direction (TD), wherein the MD is orthogonal to the TD, and the MD and TD are each orthogonal to the thickness direction. For webs, MD aligns with the long direction, and TD aligns with the width direction.

[00083] One method to produce microporous polytetrafluoroethylene (PTFE) membranes is through paste processing and expansion to form expanded polytetrafluoroethylene (ePTFE) (see Expanded PTFE Applications Handbook – Technology, Manufacturing and Applications, Ebnesajjad, Sina, (1997), Elsevier, Cambridge, MA). ePTFE is referred to herein for ease of discussion, but it is to be appreciated that expanded modified PTFE, expanded blends of PTFE, expanded copolymers of PTFE, and PTFE homopolymers are all considered to be within the purview of the invention. Patents have been issued on expandable blends of PTFE,

expandable modified PTFE, and expanded copolymers of PTFE, such as, for example, U.S. Patent No. 5,708,044 to Branca; U.S. Patent No. 6,541,589 to Baillie; U.S. Patent No. 7,531,611 to Sabol et al.; U.S. Patent No. 8,647,144 to Ford; and U.S. Patent No. 9,139,669 to Xu et al. The microporous polymer scaffold may comprise one or more fluorinated polymers selected from the group comprising: polytetrafluoroethylene (PTFE), poly(ethylene-co-tetrafluoroethylene) (PETFE), polyvinylidene fluoride (PVDF), and perfluorosulfonic acid (PFSA). Preferably, the ePTFE may be made in accordance with the teachings of U.S. Patent No. 8,757,395, which is incorporated herein by reference in its entirety, and commercially available in a variety of forms from W. L. Gore & Associates, Inc., of Elkton, MD.

[00084] One method to produce porous polyethylene membranes is through a wet or gel process known in industry. In this process, polyethylene is mixed with a hydrocarbon liquid and other additives. This mixture is heated over the polymer melt and extruded into a sheet. This sheet can then be orientated biaxially before and/or after the hydrocarbon liquid is extracted, producing a microporous membrane. Various process details are known in literature as in U.S. Patent Nos. 5,248,461, 4,873,034, 5,051,183, 6,566,012, Casting and stretching of filled and unfilled UHMW-polyethylene films, Ir.F.H. Assinck, Centre for polymers and composites, Eindhoven University of Technology, Nov 1995) and (Porous Biaxially, drawn UHMWPE Films, H.M. Fortuin, DSM Research BV, Department of Materials Technology – Fifth Int. Conf. of Environmental Ergonomics).

[00085] The microporous polymer scaffold has a first direction, a second direction and a thickness direction, wherein the first direction is orthogonal to the second direction, and the first and second directions are each orthogonal to the thickness direction.

[00086] The hydrophilic additive is deposited on the inner surfaces of the plurality of pores of the microporous polymer scaffold. The hydrophilic additive may be deposited on the surfaces of the nodes and fibrils of the microporous polymer scaffold without occluding the pores, i.e., the scaffold remains porous. The hydrophilic additive may be deposited on the surfaces of the nodes and fibrils throughout a thickness of the microporous polymer scaffold. The hydrophilic additive may be deposited on the first surface of the microporous polymer scaffold and/or the second surface of the microporous polymer scaffold.

[00087] **[Properties of the microporous polymer scaffold]**

[00088] The microporous polymer scaffold has a matrix tensile strength (MTS) in the second direction of at least about 55 MPa. The second direction is the direction in which the microporous polymer scaffold has its minimum matrix tensile strength. That is, the second direction corresponds to the direction in which the MTS of the microporous polymer scaffold is the

lowest value relative to the other directions. For microporous polymer scaffolds fabricated via a roll-to-roll process, the second direction may refer to either one of the transverse direction (TD) or the machine direction (MD), and the first direction may refer the other orthogonal direction. For instance, the first direction may refer to the TD and the second direction may refer to the MD, or vice versa. It is often the case that the MD or TD corresponds to the second direction in the microporous polymer scaffold of the present disclosure.

[00089] It is not necessary to measure the strength of the microporous polymer scaffold in every possible direction in order to determine the direction having the minimum strength. For microporous polymer scaffolds produced via a roll-to-roll process, it is typical for the minimum matrix tensile strength to align with either the MD or TD direction of the roll. Therefore, unless there is specific knowledge to the contrary, it may be presumed that the direction of minimum strength aligns with whichever direction has the lowest strength selected from TD or MD.

[00090] The microporous polymer scaffold may have a matrix tensile strength (MTS) in the second direction of at least about 60 MPa, or at least about 70 MPa, or at least about 80 MPa, or at least about 90 MPa, or at least about 100 MPa, or at least about 110 MPa, or at least about 120 MPa, or at least about 130 MPa, or at least about 140 MPa, or at least about 150 MPa, or at least about 160 MPa, or at least about 170 MPa, or at least about 180 MPa, or at least about 190 MPa, or at least about 200 MPa, or at least about 210 MPa, or at least about 220 MPa, or at least about 230 MPa, or at least about 240 MPa, or at least about 250 MPa.

[00091] The microporous polymer scaffold may have a matrix tensile strength (MTS) in the second direction of from about 55 MPa to about 425 MPa, or from about 55 MPa to about 400 MPa, or from about 80 MPa to about 400 MPa, or from about 100 MPa to about 400 MPa, or from about 120 MPa to about 400 MPa, or from about 140 MPa to about 400 MPa, or from about 160 MPa to about 350 MPa.

[00092] The matrix tensile strength (MTS) of the microporous polymer scaffold is measured as indicated in the test methods described herein.

[00093] The electrolyzer porous diaphragms of the present disclosure, comprising microporous polymer scaffolds with high MTS, have shown good handleability (e.g., as evidenced by good dimensional stability and successful assembly in liquid alkaline electrolyzers) and good electrical shorting properties (i.e., protection against electrical shorting as demonstrated, for example, by successful operation in liquid alkaline electrolyzers, and by high force-to-short values), despite being extremely thin. It is surprising that high matrix tensile strength, which is a property of the microporous polymer scaffold and that is measured in the “in-plane” direction of the microporous polymer scaffold, has enabled high shorting protection, which is

a property of the porous diaphragm and that is measured in the "thickness" direction of the diaphragm (which is also the thickness direction of the microporous polymer scaffold). This is discussed in more detail below in relation to the results of Table 2.

[00094] The microporous polymer scaffold may have a non-contact thickness of up to about 200 µm, or up to about 100 µm, or up to about 50 µm, or up to about 25 µm, or up to about 10 µm. The microporous polymer scaffold may have a non-contact thickness of any value including and between about 2 µm to about 200 µm, for example between about 2 µm and 100 µm, or about 2 µm and 50 µm, or about 2 µm and about 25 µm.

[00095] The microporous polymer scaffold may have a geometric mean MTS of at least about 90 MPa. The geometric mean MTS is defined as the square root of the product of the MTS in the first direction and the MTS in the second direction:

$$\textbf{\textit{Geometric mean MTS}} = \sqrt{(\textbf{\textit{MTS in the first direction}} \times \textbf{\textit{MTS in the second direction}})}$$

[00096] The microporous polymer scaffold may have a geometric mean MTS of at least about 100 MPa, or at least about 110 MPa, or at least about 120 MPa, or at least about 130 MPa. The microporous polymer scaffold may have a geometric mean MTS of from about 90 MPa to about 400 MPa, or from about 100 MPa to about 375 MPa, or from about 110 MPa to about 375 MPa.

[00097] The geometric mean absolute tensile strength of the microporous polymer scaffold / electrolyzer porous diaphragm contact thickness may be at least about 10 MPa. The geometric mean absolute tensile strength of the microporous polymer scaffold / electrolyzer porous diaphragm contact thickness may be at least about 15 MPa, or at least about 20 MPa, or at least about 25 MPa, or at least about 30 MPa, or at least about 35 MPa, or at least about 40 MPa, or at least about 45 MPa, or at least about 50 MPa. The geometric mean absolute tensile strength of the microporous polymer scaffold / electrolyzer porous diaphragm contact thickness may be from about 10 MPa to about 200 MPa, or from about 10 MPa to about 175 MPa, or from about 10 MPa to about 160 MPa.

[00098] The absolute tensile strength of the microporous polymer scaffold is measured as indicated in the test methods described herein.

[00099] The absolute tensile strength of the microporous polymer scaffold in the second direction / electrolyzer porous diaphragm contact thickness may be at least about 8 MPa. The absolute tensile strength of the microporous polymer scaffold in the second direction / electrolyzer porous diaphragm contact thickness may be at least about 10 MPa, or at least about 15 MPa, or at least about 20 MPa, or at least about 30 MPa, or at least about 40 MPa, or at least about 50 MPa. The absolute tensile strength of the microporous polymer scaffold in the second direction / electrolyzer porous diaphragm contact thickness may be from about 10 MPa to

about 200 MPa, or from about 15 MPa to about 200 MPa, or from about 20 MPa to about 200 MPa, or from about 30 MPa to about 200 MPa, or from about 40 MPa to about 175 MPa, or from about 50 MPa to about 175 MPa.

[000100] The microporous polymer scaffold may have a tensile strength balance ratio (absolute tensile strength in the second direction / absolute tensile strength in the first direction) of between 0.45 and 1, or between 0.50 and 1, or between 0.55 and 1, or between 0.60 and 1, or between 0.65 and 1, or between 0.70 and 1, or between 0.75 and 1, or between 0.80 and 1, or between 0.85 and 1, or between 0.90 and 1. As discussed above, a value closer to 1 is preferred because this means that the tensile strength is balanced, and therefore the tensile strengths in the first and second directions are more similar.

[000101] The microporous polymer scaffold may have a mass-per-area ranging from about 1 g/m^2 to about 60 g/m^2, or from about 2 g/m^2 to about 50 g/m^2, or from about 3 g/m^2 to about 45 g/m^2, or from about 4 g/m^2 to about 45 g/m^2, or from about 5 g/m^2 to about 45 g/m^2, or from about 6 g/m^2 to about 45 g/m^2, or from about 7 g/m^2 to about 45 g/m^2, or from about 8 g/m^2 to about 45 g/m^2. Alternatively, the microporous polymer scaffold may have a mass-per-area ranging from about 1 g/m^2 to about 35 g/m^2, or from about 2 g/m^2 to about 30 g/m^2, or from about 3 g/m^2 to about 30 g/m^2, or from about 3 g/m^2 to about 25 g/m^2. If the mass-per-area is too high, the ionic resistance of the diaphragm will be too high and it may become difficult to deposit a uniform coating of the hydrophilic additive over the microporous polymer scaffold. If the mass-per-area is too low, the handleability, gas crossover, and resistance to electrical shorting may suffer.

[000102] The mass-per-area of the microporous polymer scaffold is measured as indicated in the test methods described herein.

[000103] The microporous polymer scaffold (without the hydrophilic additive) may have a porosity of at least about 40 vol%, or at least about 75 vol%, or a porosity of at least about 80 vol%, or a porosity of at least about 85 vol%. The upper limit of porosity is not limited, but may be 95 vol%. If the porosity is too low, it will be difficult to deposit a uniform coating of the hydrophilic additive over the microporous polymer scaffold. At very low porosities, the ionic conductance of the porous diaphragm may be too low.

[000104] The porosity of the microporous polymer scaffold is measured as indicated in the test methods described herein.

[000105] The microporous polymer scaffold may have a volume-specific surface area of at least 0.5 m^2/cc or at least 1 m^2/cc or at least 5 m^2/cc or at least 10 m^2/cc. The microporous polymer

structure may have a volume-specific surface area in the range of from 0.5 to 100 m^2/cc or from 1 to 85 m^2/cc or from 5 to 70 m^2/cc or from 10 to 55 m^2/cc.

[000106] The volume-specific surface area of the microporous polymer scaffold is measured as indicated in the test methods described herein.

[000107] The microporous polymer scaffold may have an area specific true surface area of at least 5 $m^2_{surface}$/ m^2 or at least 10 $m^2_{surface}$/ m^2 or at least 25 $m^2_{surface}$/ m^2 or at least 45 $m^2_{surface}$/ m^2 or at least 50 $m^2_{surface}$/ m^2 The microporous polymer structure may have an area specific surface area in the range of from 5 to 1000 $m^2_{surface}$/ m^2 or 10 to 900 $m^2_{surface}$/ m^2 or from 25 to 800 $m^2_{surface}$/ m^2 or from 45 to 750 $m^2_{surface}$/ m^2 or from 50 to 700 $m^2_{surface}$/ m^2.

[000108] The area specific surface area of the microporous polymer scaffold is measured as indicated in the test methods described herein.

[000109] The microporous polymer scaffold may have a bubble point pressure of at least about 1 bar, or at least about 1.4 bar, or at least about 1.7 bar, or at least about 2.1 bar, or at least about 2.4 bar, or at least about 2.8 bar, or at least about 3.1 bar. The microporous polymer scaffold may have a bubble point pressure of from about 1 bar to about 5.5 bar, or from about 1 bar to about 4.8 bar, or from about 1 bar to about 4.1 bar, or from about 1 bar to about 3.4 bar, or from about 1.4 bar to about 3.4 psi, or from about 1.7 bar to about 3.4 bar. A high bubble point may result in a porous diaphragm with improved handleability and resistance to shorting, while being able to remain thin and therefore maintain low ionic resistance.

[000110] **[Hydrophilic additive]**

[000111] The hydrophilic additive is deposited on the inner surfaces of the plurality of pores of the microporous polymer scaffold.

[000112] In liquid alkaline water electrolysis, the electrolyzer porous diaphragm needs to get wet with electrolyte and stay wet, preferably totally, for low ionic resistance. The primary function of the hydrophilic additive is therefore to provide acceptable non-dewettability to the microporous polymer scaffold and therefore the electrolyzer porous diaphragm. For instance, the electrolyzer porous diaphragm may be able to maintain acceptable non-dewettability in 30% KOH (aq.) electrolyte at 90°C for its lifetime in the application. For example, a hydrophilic additive for an electrolyzer porous diaphragm for liquid alkaline water electrolysis must be durable in strong base (e.g., 30 wt% KOH in water) super-saturated with product gases such as oxygen and hydrogen and at the temperatures and time periods required for the application (e.g., about 80C-90C for up to about 10,000 hours). The hydrophilic additive is chemically stable and durable, such that it can provide a non-dewettability property even in alkaline environments. Without being bound by theory, it is believed it is critical for the

microporous polymer scaffold to be hydrophilic (and therefore acceptably non-dewettable) to prevent bubbles from the electrolyte from nucleating on and/or sticking to and therefore "blinding" the diaphragm by de-wetting, thus increasing its ionic resistance.

[000113] The content of hydrophilic additive in the porous diaphragm is not particularly limited, and may differ depending on the required degree of hydrophilicity required. The electrolyzer porous diaphragm may contain from about 2 wt% to about 95 wt% of the hydrophilic additive, or from about 5 wt% to 90 wt% of the hydrophilic additive, wherein the total weight of the porous diaphragm is 100 wt%. When the hydrophilic additive is a polymer as described below, the porous diaphragm may contain from about 2 wt% to about 25 wt% of the hydrophilic additive, or from about 3 wt% to about 20 wt% of the hydrophilic additive, or from about 3 wt% to about 15 wt% of the hydrophilic additive, or from about 3 wt% to about 12 wt% of the hydrophilic additive, or from about 4 wt% to about 11 wt% of the hydrophilic additive. When the hydrophilic additive is a ceramic as described below, the porous diaphragm may contain from about 5 wt% to about 95 wt% of the hydrophilic additive, or from about 15 wt% to about 95 wt% of the hydrophilic additive, or from about 25 wt% to about 35 wt% of the hydrophilic additive, or from about 45 wt% to about 95 wt% of the hydrophilic additive, or from about 50 wt% to about 95 wt% of the hydrophilic additive, or from about 55 wt% to about 95 wt% of the hydrophilic additive, or from about 60 wt% to about 95 wt% of the hydrophilic additive, or from about 65 wt% to about 90 wt% of the hydrophilic additive.

[000114] It may be preferred that the electrolyzer porous diaphragm resists compression under load. One way to quantify compressibility under load is by the ratio of the contact thickness, T_C, to the non-contact thickness, T_{NC} (i.e., Compressibility = $1 - T_C/T_{NC}$). The compressibility of the electrolyzer porous diaphragm as determined in this manner may be less than 1%, or less than 3%, or less than 5%, or less than 10%, or less than 15%, or less than 20%, or less than 25%, or less than 30%, or less than 40%, or less than 50%, or less than 60%, or less than 70%, or less than 80%.

[000115] The hydrophilic additive is not particularly limited and any suitable additives known in the art may be used. The hydrophilic additive may comprise a polymer or ceramic. One or more hydrophilic additives may be deposited on the inner surfaces of the plurality of pores. For instance, the microporous polymer scaffold may have both a polymer and ceramic deposited thereon, or two or more polymers deposited thereon, or two or more ceramics deposited thereon, or any number of polymers and ceramics deposited thereon.

[000116] The polymer may be an ionomer. The ionomer may be selected from an anion exchange ionomer and a cation exchange ionomer, optionally wherein the ionomer is perfluorinated,

partially fluorinated, or non-fluorinated. The ionomer may comprise heteroatoms other than fluorine. The ionomer may comprise aromatic moieties and/or non-aromatic (e.g., aliphatic or olefinic) moieties. The ionomer may be a perfluorosulfonic acid or a salt of a perfluorosulfonic acid (i.e., a PFSA ionomer, or salt thereof). The PFSA ionomer may have an equivalent weight (EW) of from about 500 to about 1100 g/eq, or from about 700 to about 850 g/eq.

[000117] The ceramic may be a sub-micron particle or nanomaterial and may comprise a wide variety of materials including glasses. Examples of suitable ceramics include silica, alumina, titania, ceria, zirconia, yttria-stabilized zirconia (such Nyacol ZRYS3), other oxides (such as metal oxides), and other classes of ceramics including carbides, nitrides, sulfides, borides, phosphides, selenides, titanates, carbonates, nitrates, sulfates, borates, and phosphates.

[000118] In the context of the present disclosure, the hydrophilic additive being deposited on the inner surfaces of the plurality of pores means that the hydrophilic additive is present on the surfaces of the pores. The surfaces of the pores may be fully covered by the hydrophilic additive, or at least partially covered by the hydrophilic additive.

[000119] **[Method of producing the porous diaphragm]**

[000120] Fabricating an electrolyzer porous diaphragm by providing a microporous polymer scaffold and depositing the hydrophilic additive in the pores of the microporous polymer scaffold may be preferred over other methods (e.g., incorporation of the hydrophilic additive via co-extrusion of the hydrophilic additive and a polymeric binder, or co-deposition of the hydrophilic additive and a hydrophilic binder) because, for example, the strength of the electrolyzer porous diaphragm (e.g., the tensile strength of the porous diaphragm per unit of mass or per unit thickness) may be increased. The electrolyzer porous diaphragm may be produced by incorporating the hydrophilic additive into the microporous polymer scaffold via a method that comprises imbibing. As used herein, the term “imbibing” refers to a process of depositing a material within the pores of a microporous scaffold using a liquid carrier, but not substantially incorporating the imbibed material into the matrix of the microporous polymer scaffold, such that the microporous scaffold remains largely intact. For example, the microporous polymer scaffold may be wetted with an imbibing fluid, wherein the imbibing fluid comprises the hydrophilic additive and a liquid carrier. To achieve a high loading of hydrophilic additive in the electrolyzer porous diaphragm, a high concentration of hydrophilic additive in the imbibing fluid may be preferred (e.g., the imbibing fluid may be prepared with minimal dilution of the hydrophilic additive). As used herein, a microporous polymer scaffold that is “wetted” with a fluid has some or all of its pores filled with the fluid. The wetted

microporous polymer scaffold may then be dried, such that the liquid carrier is substantially removed, resulting in the hydrophilic additive being deposited within the pores of the microporous polymer scaffold. The imbibed microporous polymer scaffold may be dried by heating the scaffold to a high temperature, such as to 250°C, for a sufficient period of time, such as 1 minute to 120 minutes. It will be appreciated by one of ordinary skill in the art that other conventional drying methods may be used, and that drying conditions, in particular time and temperature, may be modified depending on the needs of the process and on the limitations of the materials (e.g., including their melting points and/or glass transition temperatures and/or decomposition temperatures). The method may further comprise a step of heat treating the dried imbibed microporous polymer scaffold.

[000121] The hydrophilic additive may be imbibed from one side of the microporous polymer scaffold (e.g., by applying a thin film of the imbibing fluid on one side of the microporous polymer scaffold via Mayer bar coating), or from both sides (first and second surfaces) of the microporous polymer scaffold (e.g., by dip coating the microporous polymer scaffold in the imbibing fluid). The microporous polymer scaffold imbibed with the hydrophilic additive is not occluded such that it remains porous, and thus may be considered a porous diaphragm. The hydrophilic additive may be imbibed such that it is substantially contained within the pores of the microporous polymer scaffold (i.e., the thickness of hydrophilic additive deposited on the first or second surface of the microporous polymer scaffold, outside the pore volume of the microporous polymer scaffold, sometimes referred to as “buttercoat” layers, is minimal). The thickness of a minimal buttercoat layer may be less than 2 micrometers, or less than 1 micrometer, or less than 0.5 micrometers, or less than 0.2 micrometers, or less than 0.1 micrometers.

[000122] The imbibing process may comprise a backer, which is a film or fabric, such as a woven material or a non-woven material, such as a web, that serves as a processing aid in the production of the porous diaphragm by physically supporting it through at least a portion of the imbibing process.

[000123] The use of a backer may enable a higher loading of hydrophilic additive in the microporous polymer scaffold. The backer may be a polymer film. The imbibing process may comprise a step in which the microporous polymer scaffold wetted with imbibing fluid is in contact with the backer. The backer may be adhered to the diaphragm, and the force of adhesion may be such that the backer can be removed from (e.g., peeled off of) the diaphragm without substantially damaging the diaphragm.

[000124] The liquid carrier in the imbibing fluid is not particularly limited, and any suitable liquid carriers known in the art may be used. Suitable liquid carriers may include water and organic liquids. Organic liquids may include alcohols and mixtures of alcohols (such as a C1-C5 alcohol), dimethyl sulfoxide, dimethyl acetamide, acetonitrile, toluene, DMAc, MEK, acetone, DMF, THF, and NMP. More than one liquid carrier may be used, such as two, or three, or four liquid carriers. The C1-C5 alcohol may be any one selected from methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol, pentan-1-ol, and a combination thereof.

[000125] If the imbibing fluid does not spontaneously and readily wet the microporous polymer scaffold, then a variety of techniques may be employed to assist in achieving good wetting, such as by applying a differential pressure to force the liquid into the microporous polymer scaffold, raising the temperature of the fluid to lower its viscosity and surface tension, and/or pre-wetting the microporous polymer scaffold with another miscible liquid. As described above, imbibing microporous polymer scaffolds, especially low surface energy scaffolds, relies on good wetting. "Wetting" results when the contact angle, θ, between the liquid and the solid scaffold is less than about 90 degrees. Spontaneous wetting occurs when the surface energy between the solid and liquid, γ_{SL} is less than the surface energy between the solid and air, γ_{SA}. The relationship between these parameters and the liquid-air surface energy, γ_{LA} (i.e., the surface tension of the liquid), is given by the relationship below:

$$\gamma_{SL} = \gamma_{SA} - \gamma_{LA} * \cos(\theta)$$

[000126] To achieve good wetting, the surface tension of the imbibing fluid should be sufficiently low to penetrate the microporous polymer scaffold. For example, a surface tension of less than or equal to about 30 dynes/cm is typically required to penetrate expanded microporous PTFE. Higher surface tension imbibing fluids may accordingly be suitable for higher energy scaffolds such as microporous polyethylene or microporous polypropylene.

[000127] Imbibing fluids that are aqueous or substantially aqueous (i.e. that comprise water as a liquid carrier) are preferred in some cases, for example because of the availability of stable and highly concentrated colloidal dispersions, or because of safety and environmental reasons. To enable an aqueous or substantially aqueous imbibing fluid to wet a microporous polymer scaffold with minimal dilution, a suitable wetting agent may be emulsified in the aqueous or substantially aqueous imbibing fluid with the aid of a surfactant to provide an aqueous system. Suitable wetting agents include alcohols and mixtures of alcohols that exhibit a low water solubility, such as those alcohols having five to ten carbon atoms in the longest continuous chain, e.g., alcohols with C5-C10 linear chains, and the like. For example, pentanols, hexanols, octanols, and the like, are within the range of suitable wetting agents. Herein, these wetting

agents may be referred to as “insoluble alcohols.” Similarly, suitable wetting agents also include carboxylic acids and mixtures of carboxylic acids that exhibit a low water solubility, such as those carboxylic acids having five to ten carbon atoms in the longest continuous chain, e.g., carboxylic acids with C5-C10 linear chains, and the like. For example, pentanoic acid, hexanoic acid, octanoic acid, and the like, are within the range of suitable wetting agents. Herein, these wetting agents may be referred to as “insoluble carboxylic acids.”. Such insoluble wetting agents are present in the imbibing fluid above their solubility limit so as to form an “oil phase” that may be emulsified. Further, the imbibing fluid can incorporate with the water insoluble alcohol(s) and/or carboxylic acid(s) other water insoluble organics, such as alkanes, etc. Optionally, the wetting agent may also exhibit a low γ_{SL} relative to the targeted low surface energy scaffold.

[000128] The surfactant(s) can be a single surfactant or a combination of surfactants. Suitable surfactants are defined as those that are able to emulsify the desired wetting agent. For example, for the alcohols described above, several classes of anionic surfactants can be used, including, but not limited to, those having a structure of $R(EO)_nOSO_3^-$ or $ROSO_3^-$ where R can be any organic chain, "O" is oxygen, "S" is sulfur, "EO" is ethylene oxide and $n \geq 1$. In an alternate embodiment, nonionic surfactants having the structure $R(EO)_nOH$, where $n \geq 1$, are also suitable for this invention, in which “EO” is ethylene oxide. In a preferred embodiment, nonionic surfactants with hydrophilic-lipophilic balance ("HLB") values of ten or greater were found most effective to emulsify the wetting agents described above. The concentration of surfactant can be adjusted in order to achieve good emulsification of the desired wetting agent. For example, when 4% by weight of hexanol wetting agent (based on the total aqueous solution weight) is used, a concentration of about 2% of sodium dodecyl ether sulfate was found to be suitable. In an alternate formulation, 6% wt. of an ethoxylated alcohol was able to emulsify 4% wt. hexanol wetting agent. Other examples of suitable surfactants include Tergitol TMN10 and Barlox 8S.

[000129] In addition to the surfactant and the wetting agent, a stabilizing agent can optionally be added. A stabilizing agent is typically soluble in both the wetting agent and water, and it allows a greater amount of wetting agent to be stabilized in the aqueous system than without the stabilizer. In one embodiment, glycols were found to be effective stabilizers, such as but not limited to dipropylene glycol ("DPG"), dipropylene glycol monomethyl ether, and propylene glycol. A wide range of stabilizer concentrations can be used depending on the amount of additional stability desired. For instance, if a small increase in stability is desired, a small amount of the optional stabilizer should be used. Conversely, higher stabilizer concentrations

generally further increase the emulsion stability. Exceptions to these general guidelines do however exist. For example, DPG may be an effective stabilizer when used in concentrations ranging from less than about 1% wt. up to about 10% wt. based on total aqueous emulsion weight for hexanol-based systems.

[000130] The amount of the hydrophilic additive in the fluid may be from 0.5 mass% to 75 mass%, depending on the hydrophilic additive and the desired loading of hydrophilic additive in the porous diaphragm.

[000131] When the hydrophilic additive is an ionomer such as perfluorosulfonic acid polymer, the liquid carrier may preferably comprise water and a C1-C5 alcohol such as ethanol.

[000132] When the hydrophilic additive is a ceramic such as a metal oxide, the liquid carrier may preferably comprise water.

[000133] The hydrophilic additive may exist in the imbibing fluid in various forms, for example the hydrophilic additive may be dissolved, mixed, dispersed, or suspended in the liquid carrier. The imbibing fluid may therefore be a suspension or a colloidal dispersion. When the imbibing fluid is a suspension or a colloidal dispersion, it may contain additives such as dispersing agents to stabilize the suspension or colloidal dispersion. The purpose of such dispersing agents is typically to reduce viscosity, reduce or prevent agglomeration of particles, and/or reduce or prevent settling of particles. Preparation of the suspension or colloidal dispersion, and maintaining the particles as suspended or dispersed, may require the use of high-shear mixing. Various means of high-shear mixing for the preparation of suspensions and colloidal dispersions are available and are well-known to those of ordinary skill in the art, such as rotor-stators, Cowles mixers, wet jet mills, media mills, and so on.

[000134] **[Electrolyzer]**

[000135] The present disclosure provides an electrolyzer comprising: an anode; a cathode; the electrolyzer porous diaphragm as described herein; and a liquid electrolyte, wherein the electrolyzer porous diaphragm is positioned between the anode and the cathode, and wherein the liquid electrolyte at least partially wets the electrolyzer porous diaphragm.

[000136] The electrolyzer is a gas-generating device (i.e., a device where the intended function comprises gas evolution at one or both electrodes). In the present context, a device that generates gas only as a result of an unintended side reaction or during “upset” conditions (e.g., a lithium ion battery) is not considered a gas-generating device as defined herein. In a gas-generating device, low gas permeance is desirable to prevent gas-crossover across the diaphragm.

[000137] The electrolyzer may be a water electrolyzer in which water electrolysis may occur. The electrolyzer may be a liquid alkaline water electrolyzer. A high loading of hydrophilic additive in the electrolyzer porous diaphragm (i.e., deposited within the pore volume of the microporous polymer scaffold) may be preferred (e.g., to prevent or minimize the ionic resistance of the porous diaphragm from increasing due to electrolyte de-wetting from the porous diaphragm). A low liquid permeance through the electrolyzer porous diaphragm may also be preferred (e.g., to minimize electrolyte flow in the case of a pressure gradient across the porous diaphragm).

[000138] The electrolyte in a water electrolyzer may be a liquid alkaline electrolyte. The liquid alkaline electrolyte may comprise a strong base. The liquid alkaline electrolyte may comprise sodium hydroxide or potassium hydroxide. The concentration of strong base in the electrolyte may be at least 5 wt%, at least 10 wt%, at least 15 wt%, at least 20 wt%, at least 25 wt%, or at least 30 wt%. The porous diaphragm may be wetted with the electrolyte to enable ion conduction through the thickness of the porous diaphragm. An alkaline electrolyte may have a pH greater than 7, or greater than about 8, or greater than about 9, or greater than about 10, or greater than about 11, or greater than about 12, or greater than about 13, or greater than about 14.

[000139] In a liquid alkaline water electrolyzer, the porous diaphragm is positioned between the anode and cathode in order to prevent electrical shorting (the porous diaphragm is non-conductive to electrons) and to separate product gases formed at the anode and cathode.

[000140] The anode is not particularly limited and any known suitable anode materials in the art may be used. The anode may comprise any one selected from nickel, cobalt and iron. The cathode is not particularly limited and any known suitable cathode materials in the art may be used. The cathode may comprise any one selected from nickel, platinum and carbon.

[000141] The liquid alkaline electrolyte at least partially wets the porous diaphragm so that the diaphragm is conductive to ions, specifically hydroxide ions. The liquid alkaline electrolyte may fully wet the porous diaphragm. The liquid alkaline electrolyte is not particularly limited and any known suitable liquid alkaline electrolyte may be used. The liquid alkaline electrolyte may be an aqueous or substantially aqueous alkaline solution i.e. the liquid alkaline electrolyte comprises water. The liquid alkaline electrolyte may comprise a metal hydroxide, and the metal hydroxide may be sodium hydroxide or potassium hydroxide.

[000142] **[Use of the porous diaphragm or electrolyzer]**

[000143] As described above, when used in the electrolysis of water, the microporous polymer scaffold and the hydrophilic additive should be base-stable because alkaline electrolyte is used.

[000144] **[Test methods]**

[000145] These test methods relate to the above description and the examples section below.

[000146] **Non-contact thickness (e.g. microporous polymer scaffold):**

[000147] A sample of microporous polymer scaffold was placed over a flat smooth metal anvil and tensioned to remove wrinkles. The height of the microporous polymer structure on the anvil was measured and recorded using a non-contact Keyence LS-7010M digital micrometer. Next, the height of the anvil without the microporous polymer scaffold was recorded. The thickness of the microporous polymer scaffold was taken as a difference between micrometer readings with and without the microporous polymer scaffold being present on the anvil.

[000148] **Contact thickness (e.g. electrolyzer porous diaphragm):**

[000149] A sample of electrolyzer porous diaphragm was analyzed with a Mitutoyo Litematic handheld micrometer with a measuring force of 0.01 Newtons to determine the contact thickness.

[000150] **Matrix tensile strength of the microporous polymer scaffold (first and second directions):**

[000151] The absolute tensile strength was normalized to discount pore volume to determine the matrix tensile strength of the microporous polymer scaffold, which exclusively accounts for strength-contributing components when determining the tensile strength of a porous material. It was calculated by dividing the tensile strength of the sample by a ratio of its bulk density and the skeletal density of the strength-contributing component as shown in the following formula:

[000152] *Matrix Tensile Strength = (Absolute Tensile Strength/Non-Contact Thickness)/(Bulk Density/Skeletal Density)* [MPa]

[000153] **Absolute tensile strength (e.g. microporous polymer scaffold and electrolyzer porous diaphragm (first and second directions)):**

[000154] The tensile strength was determined in each direction by measuring the maximum tensile load of a sample using ASTM D638-5, then dividing the load by the original gauge width of the sample.

[000155] **Mass-per-area (e.g. microporous polymer scaffold):**

[000156] The microporous polymer scaffold was strained sufficiently to eliminate wrinkles, and then a 10 cm^2 piece was cut out using a die. The 10 cm^2 piece was weighed on a conventional laboratory scale. The mass-per-area (M/A) was then calculated as the ratio of the measured mass to the known area. This procedure was repeated 2 times and the average value of the M/A was calculated.

[000157] **Bulk density (e.g. microporous polymer scaffold):**

[000158] The bulk density of the microporous polymer scaffold was calculated by dividing its mass-per-area by its non-contact thickness.

[000159] **Skeletal density of the microporous polymer scaffold:**

[000160] The skeletal density is the density of a solid calculated by excluding all open pores and internal void volume. A Micromeritics AccuPyc II 1340 Gas Pycnometer (Micromeritics Instrument Corp., Norcross, GA) using helium gas as the displacement medium was used to analyze the samples. The AccuPyc uses the theory of gas displacement to determine the volume occupied by a given sample. The sample was added to a 3.5 cm^3 sample cup and sealed in the analysis chamber. The sample was purged 50 times with helium gas at 19.5 psig and the gas expands into another precision internal volume. Once purged, the sample was then analyzed with 15 cycles of fill cycles at 19.5 psig, or until the sample volume equilibrium was detected (0.02% precision). The skeletal density was calculated by dividing the sample mass by the adjusted sample volume. The sample mass was determined by weighing on an analytical balance of +/- 0.1 mg sensitivity.

[000161] Sample Skeletal Density = Sample Mass / Sample Volume

[000162] Sample Volume = Sample Chamber Volume - (Expansion Chamber Volume/((Gauge Pressure After Fill/Gauge Pressure After Expansion) - 1))

[000163] **Porosity of the microporous polymer scaffold:**

[000164] The porosity of the microporous polymer scaffold was calculated by dividing the difference between skeletal density and bulk density of the scaffold by the skeletal density of the scaffold per the following formula:

[000165] Porosity = ((Skeletal Density – Bulk Density)/Skeletal Density)*100% [Vol%]

[000166] **Specific surface area of the microporous polymer scaffold:**

[000167] The surface area per unit mass, expressed in units of m^2/g, of the sample was measured using the Brunauer-Emmett-Teller (BET) method on a Quantachrome NOVAtouch LX4 Gas Sorption System (Quantachrome Instruments – Anton Paar – Boynton Beach, FL). A sample was cut from the center of the sample sheet and placed into a Type B long cell, 9 mm LG bulb (reference number 193885). The mass of the sample was approximately 0.1 to 0.2 grams. The tube was placed into the Coulter SA-Prep Surface Area Outgasser, (Model SA-PREP, P/N 5102014) from Beckman Coulter Inc., Fullerton, CA and purged at room temperature for 2 hours with helium. The sample tube was then removed from the SA-Prep Outgasser and weighed. A glass filler rod (reference number 193900) was placed in the cell and the assembly was then placed into the NOVAtouch LX4 Gas Sorption System and the BET surface area

analysis was run in accordance with the instrument instructions using helium to calculate the free space and nitrogen as the adsorbate gas. A single BET surface area (m^2/g) measurement was recorded for each sample.

[000168] **Volume-specific surface area of the microporous polymer scaffold**

[000169] The specific surface area of the microporous polymer scaffold was normalized to account for differences in polymer densities by multiplying by the skeletal density of the microporous polymer scaffold:

[000170] Volume-specific surface area ($m^2_{surface}/cc$) = Specific surface area ($m^2_{surface}/g$) * Skeletal density (g/cc)

[000171] **Area specific surface area of the microporous polymer scaffold**

[000172] The area specific true surface area of the microporous polymer scaffold was calculated by multiplying its specific surface area by its mass per area:

[000173] Area specific surface area ($m^2_{surface}/m^2$) = Specific surface area ($m^2_{surface}/g$) * Mass per area (g/m^2)

[000174] **Bubble point:**

[000175] The bubble point was measured according to the general teachings of ASTM F316-03 using a Capillary Flow Porometer (Model 3G zh from Quantachrome Instruments). The sample holder comprised a porous metal plate (Part Number: 196450, Anton Paar), 25.4 mm in diameter and a plastic mask (Part Number ABF-300, Professional Plastics), 18 mm inner diameter x 24.5 mm outer diameter. The sample was placed in between the metal plate and the plastic mask. The sample was then clamped down and sealed using an O-ring (Part Number: 193798, Anton Paar). The sample was wet with the test fluid (Silicone fluid, 10 cSt, having a surface tension of 19.75 dynes/cm)

[000176] **Ex-situ ionic resistance of the electrolyzer porous diaphragm:**

[000177] Ex-situ ionic resistance was measured using SS disk electrodes, a portable potentiostat, and a conductivity standard. A 40 mm electrolyzer porous diaphragm sample was punched with a die, wet with isopropyl alcohol, and placed into a jar with 10000 µS conductivity standard (Fisher Scientific 15-077-952) for at least 1 hour. The sample was then placed on the 50 mm bottom disk electrode, which has a 5 mm lip to hold a small pool of solution. After 1 mL of additional solution was added on the electrolyzer porous diaphragm, the 20 mm diameter top electrode, wrapped in about 5 mm thick PTFE was placed on top, with an approximately 1 kg hollow cylindrical weight to hold the electrode in place. Leads from a portable potentiostat (PalmSens Sensit BT) were attached to the top and bottom electrode. Using PSTrace software, an Impedance Spectroscopy measurement was taken from 15 kHz to 150 kHz. In JMP®Pro

16.1.0, a line was fit to the Z_{real} and $-Z_{imag}$ to estimate the Z_{real} intercept, which was recorded as the ex-situ ionic resistance.

[000178] **Electrolyzer porous diaphragm polarization curve slope:**

[000179] Polarization curve slopes were measured on a 10 cm^2 electrolyzer porous diaphragm sample using Electrocell hardware. A zero-gap arrangement was achieved with a series of EPDM and PTFE gaskets and spacers. Nickel felt (Baekert) was used as both the anode and cathode and nickel foam was used as a compressible porous transport layer. The resultant cell was operated at atmospheric pressure, at 80 °C, and with a 30 wt% aqueous KOH electrolyte. The cell was preconditioned for two minutes each at applied current densities of 50, 300, 600, 1000, 600, 300, 50 mA/cm^2 for a total of 5 cycles, then 15 minutes at 50 mA/cm^2 and 15 minutes at 600 mA/cm^2.

[000180] Two polarization curves were generated by applying current density setpoints of 5, 10, 20, 30, 40, 50, 75, 100, 150, 200, 250, 300, 350, 400, 450, 500, 600, 700, 800, 900, 1000 mA/cm^2 for two minutes each in ascending, then descending order. Polarization curves were generated using the average voltage over the last 30 seconds at each current density. Polarization curve slopes were generated using a fit line on the region from 500-1000 mA/cm^2 of the descending polarization curves.

[000181] **Electrolyzer porous diaphragm alkaline stability:**

[000182] An electrolyzer porous diaphragm sample was submerged in a lidded beaker containing 500 mL of 30 wt% aqueous potassium hydroxide and heated on a hot plate to 80°C under stirring. The sample was conditioned in this setup for a time relevant to the application, then removed, rinsed 4 times in RO water, dried, and evaluated for properties relevant to the application. Examples of relevant times may include 24 hours, 1 week, 1 month, up to 3 months, up to 6 months, and up to 1 year. These relevant times are in general shorter than the expected lifetime of the electrolyzer porous diaphragm in use and are intended to provide directional feedback to inform, for example, the development, qualification, and quality control of materials. An electrolyzer porous diaphragm for liquid alkaline water electrolysis may be expected to last 5-10 years in operation.

[000183] **Force to short of an electrolyzer porous diaphragm:**

[000184] Shorting protection for an electrolyzer porous diaphragm was measured using a Universal Instron® test system with a 100 lbf load cell, an integrated Keithley 580 Micro-Ohmmeter, and 14 mm diameter test probes. The Bottom Probe is flat, while the Top Probe is rounded (i.e., approximately hemispherical) as shown in Figure 4. An electrolyzer porous diaphragm sample was cut to approximately 1x1 inches and placed on the bottom probe. An example electrode,

40x40 stainless steel square mesh with a wire diameter of 0.0065", available from McMaster-Carr®, was cut to about 0.5x0.5 inches and placed on the top surface of the diaphragm. The Top Probe was lowered at a rate of 0.1 mm per second while the resistance between probes was measured. When the resistance dropped to below overload (200 kOhm), the force was recorded as the Force-to-Short.

[000185] **Liquid Permeance of the electrolyzer porous diaphragm**

[000186] A 50 mm diameter sample of electrolyzer porous was cut and placed inside a METcell 2-inch Crossflow cell from Evonik (parts METXF-2.5-136 and METXF-2.5-137) liquid flow cell. A layer of hydrophilic PVDF membrane (part GVWP04700 from Millipore Sigma) was placed in between the sample and the metal frit support to prevent damage to the sample. Isopropyl alcohol was pressurized to between 1-50 bar via a head of pressurized nitrogen and flowed through the sample for 30 minutes. The pressure is selected to provide a reasonable test time for a particular sample and the measurements are carried out at ambient temperature. The permeate alcohol was collected at the outlet of the cell in a flask and its mass measured on a conventional laboratory scale to determine the permeance of the sample per the following equation:

[000187] Permeance = Permeate Mass/Permeate Density/((Sample Diameter/2)^2*pi)/Flow Time/Pressure

[000188] **[Examples]**

[000189] The present disclosure will be described in more detail with reference to Examples. The present disclosure is not limited to the following Examples.

[000190] **[Example 1]**

[000191] A microporous PTFE scaffold known in the art, where PTFE fine powder based on teachings by U.S. Pat. No. 6,541,589, was processed into scaffolds through process methods known to those skilled in the art following the teaching of U.S. Patent 3,953,566 to Gore. The resulting microporous polymer scaffold "A" had the properties described in Table 1.

[000192] A single layer of the microporous polymer scaffold was restrained and then coated from both sides with a liquid composition comprising 3 mass% perfluorosulfonic acid polymer (equivalent weight 800 g/eq), 9.9 mass% water, and 87.1 mass% ethanol. The wet microporous polymer scaffold was then immersed in an aqueous bath containing 25 mass% sodium chloride (coacervation according to teachings of US5718947A) then rinsed with water and dried at 125°C. The coated scaffold was annealed at 160°C for 30 minutes. The resulting electrolyzer porous diaphragm had the properties described in Table 2.

[000193] **[Example 2]**

[000194] A microporous PTFE scaffold was produced by practicing the following steps in sequence: A fine powder PTFE resin was mixed with a lubricant Isopar K in the proportion of 130 cc/lb. The mixture was compressed into a cylindrical shape and paste extruded into a tape at a reduction ratio of 70:1. The tape was calendered decreasing its thickness by a ratio of 2.5:1. The tape was dried and then longitudinally stretch at 300°C at a ratio of 11:1. It was then heat treated at 347°C and stretched transversely at 330°C at a ratio of 21:1 and finally restrained for heat treatment at 365°C. The resulting microporous polymer scaffold "B" had the properties described in Table 1.

[000195] A substantially aqueous imbibing dispersion was prepared comprising yttria-stabilized zirconia nanoparticles (ZRYS3 available from Nyacol Nano Technologies, Inc.). The nanoparticles are nominally 3 mol% yttria, 32 nanometers in diameter, and the as-received dispersion is 52 mass% in water. To the as-received dispersion, 2 mass% 1-hexanol and 2 mass% Tergitol TMN-10 were added, and the mixture was agitated to emulsify the 1-hexanol. A single layer of microporous polymer scaffold was restrained and then imbibed from both sides with the imbibing dispersion. Excess imbibing dispersion was carefully removed from the surfaces of the microporous polymer scaffold by wiping with a lint-free cloth. The microporous polymer scaffold was then dried with a heat gun set to 125°C until visibly dry (up to about 1 minute), and then heat treated in a hot air convection oven at 150°C for an additional hour. The resulting electrolyzer porous diaphragm had the properties described in Table 2.

[000196] **[Example 3]**

[000197] A microporous PTFE scaffold was produced as described in Example 2. The resulting microporous polymer scaffold "B" had the properties described in Table 1.

[000198] A substantially aqueous imbibing dispersion was prepared comprising yttria-stabilized zirconia nanoparticles (ZRYS3 available from Nyacol Nano Technologies, Inc.). The nanoparticles are nominally 3 mol% yttria, 32 nanometers in diameter, and the as-received dispersion is 52 mass% in water. To the as-received dispersion, 2 mass% 1-hexanol and 2 mass% Tergitol TMN-10 were added, and the mixture was agitated to emulsify the 1-hexanol. 2 layers of microporous polymer scaffold were restrained and then imbibed from both sides with the imbibing dispersion. Excess imbibing dispersion was carefully removed from the surfaces of the microporous polymer scaffold by wiping with a lint-free cloth. The microporous polymer scaffolds were then dried with a heat gun set to 125°C until visibly dry (up to about 1 minute), leading the dispersion to create a bond between the layers, and then heat treated in a hot air

convection oven at 150°C for an additional hour. The resulting electrolyzer porous diaphragm had the properties described in Table 2.

[000199] **[Example 4]**

[000200] A microporous PTFE scaffold was produced as described in Example 2. The resulting microporous polymer scaffold "B" had the properties described in Table 1.

[000201] A substantially aqueous imbibing dispersion was prepared comprising yttria-stabilized zirconia nanoparticles (ZRYS3 available from Nyacol Nano Technologies, Inc.). The nanoparticles are nominally 3 mol% yttria, 32 nanometers in diameter, and the as-received dispersion is 52 mass% in water. To the as-received dispersion, 2 mass% 1-hexanol and 2 mass% Tergitol TMN-10 were added, and the mixture was agitated to emulsify the 1-hexanol. 3 layers of microporous polymer scaffold were restrained and then imbibed from both sides with the imbibing dispersion. Excess imbibing dispersion was carefully removed from the surfaces of the microporous polymer scaffold by wiping with a lint-free cloth. The microporous polymer scaffolds were then dried with a heat gun set to 125°C until visibly dry (up to about 1 minute), leading the dispersion to create a bond between the layers, and then heat treated in a hot air convection oven at 150°C for an additional hour. The resulting electrolyzer porous diaphragm had the properties described in Table 2.

[000202] **[Example 5]**

[000203] A microporous PTFE scaffold was produced as described in Example 2. The resulting microporous polymer scaffold "B" had the properties described in Table 1.

[000204] A substantially aqueous imbibing dispersion was prepared comprising yttria-stabilized zirconia nanoparticles (ZRYS3 available from Nyacol Nano Technologies, Inc.). The nanoparticles are nominally 3 mol% yttria, 32 nanometers in diameter, and the as-received dispersion is 52 mass% in water. To the as-received dispersion, 2 mass% 1-hexanol and 2 mass% Tergitol TMN-10 were added, and the mixture was agitated to emulsify the 1-hexanol. 4 layers of microporous polymer scaffold were restrained and then imbibed from both sides with the imbibing dispersion. Excess imbibing dispersion was carefully removed from the surfaces of the microporous polymer scaffold by wiping with a lint-free cloth. The microporous polymer scaffolds were then dried with a heat gun set to 125°C until visibly dry (up to about 1 minute), leading the dispersion to create a bond between the layers, and then heat treated in a hot air convection oven at 150°C for an additional hour. The resulting electrolyzer porous diaphragm had the properties described in Table 2.

[000205] **[Example 6]**

[000206] A microporous PTFE scaffold was produced as described in Example 2. The resulting microporous polymer scaffold "B" had the properties described in Table 1.

[000207] A substantially aqueous imbibing dispersion was prepared comprising yttria-stabilized zirconia nanoparticles (ZRYS3 available from Nyacol Nano Technologies, Inc.). The nanoparticles are nominally 3 mol% yttria, 32 nanometers in diameter, and the as-received dispersion is 52 mass% in water. To the as-received dispersion, 2 mass% 1-hexanol and 2 mass% Tergitol TMN-10 were added, and the mixture was agitated to emulsify the 1-hexanol. 8 layers of microporous polymer scaffold were restrained and then imbibed from both sides with the imbibing dispersion. Excess imbibing dispersion was carefully removed from the surfaces of the microporous polymer scaffold by wiping with a lint-free cloth. The microporous polymer scaffolds were then dried with a heat gun set to 125°C until visibly dry (up to about 1 minute), leading the dispersion to create a bond between the layers, and then heat treated in a hot air convection oven at 150°C for an additional hour. The resulting electrolyzer porous diaphragm had the properties described in Table 2.

[000208] **[Example 7]**

[000209] A microporous PTFE scaffold was made in a similar manner to example Examples 2-6, except consisting of 2 layers of tape that were combined at the calendering step. The resulting microporous polymer scaffold "I" had the properties described in Table 1.

[000210] A single layer of microporous polymer scaffold was restrained and then coated from both sides with a liquid composition comprising 3 mass% perfluorosulfonic acid polymer (equivalent weight 800 g/eq), 9.9 mass% water, and 87.1 mass% ethanol. The wet microporous polymer scaffold was dried at 100°C and then annealed at 160°C for 30 minutes.

[000211] A substantially aqueous imbibing dispersion was prepared comprising yttria-stabilized zirconia nanoparticles (ZRYS3 available from Nyacol Nano Technologies, Inc.). The nanoparticles are nominally 3 mol% yttria, 32 nanometers in diameter, and the as-received dispersion is 52 mass% in water. To the as-received dispersion, 2 mass% 1-hexanol and 2 mass% Tergitol TMN-10 were added, and the mixture was agitated to emulsify the 1-hexanol. The composite scaffold was restrained and then imbibed from both sides with the imbibing dispersion. Excess imbibing dispersion was carefully removed from the surfaces of the microporous polymer scaffold by wiping with a lint-free cloth. The microporous polymer scaffold was then dried with a heat gun set to 125°C until visibly dry (up to about 1 minute), and then heat treated in a hot air convection oven at 150°C for an additional hour. The resulting electrolyzer porous diaphragm had the properties described in Table 2.

[000212] **[Example 8]**

[000213] A microporous PTFE scaffold was made in a similar manner to Example 7, in which 2 layers of tape were combined at the calendering step. The resulting microporous polymer scaffold "I" had the properties described in Table 1.

[000214] Two layers of microporous polymer scaffold were restrained and then coated from both sides with a liquid composition comprising 3 mass% perfluorosulfonic acid polymer (equivalent weight 800 g/eq), 9.9 mass% water, and 87.1 mass% ethanol. The wet microporous polymer scaffold was then dried with a heat gun set to 100°C until visibly dry (up to about 1 minute), leading the coating to create a bond between the layers, and then annealed at 160°C for 30 minutes resulting in a composite scaffold.

[000215] A substantially aqueous imbibing dispersion was prepared comprising yttria-stabilized zirconia nanoparticles (ZRYS3 available from Nyacol Nano Technologies, Inc.). The nanoparticles are nominally 3 mol% yttria, 32 nanometers in diameter, and the as-received dispersion is 52 mass% in water. To the as-received dispersion, 2 mass% 1-hexanol and 2 mass% Tergitol TMN-10 were added, and the mixture was agitated to emulsify the 1-hexanol. The composite scaffold was restrained and then imbibed from both sides with the imbibing dispersion. Excess imbibing dispersion was carefully removed from the surfaces of the microporous polymer scaffold by wiping with a lint-free cloth. The microporous polymer scaffold was then dried with a heat gun set to 125°C until visibly dry (up to about 1 minute), and then heat treated in a hot air convection oven at 150°C for an additional hour. The resulting electrolyzer porous diaphragm had the properties described in Table 2.

[000216] **[Example 9]**

[000217] An ultrahigh molecular weight PE microporous polymer scaffold was made using a gel process. The resulting microporous polymer scaffold "F" had the properties described in Table 1.

[000218] A substantially aqueous imbibing dispersion was prepared comprising yttria-stabilized zirconia nanoparticles (ZRYS3 available from Nyacol Nano Technologies, Inc.). The nanoparticles are nominally 3 mol% yttria, 32 nanometers in diameter, and the as-received dispersion is 52 mass% in water. To the as-received dispersion, 2 mass% 1-hexanol and 2 mass% Tergitol TMN-10 were added, and the mixture was agitated to emulsify the 1-hexanol. A layer of microporous polymer scaffold was restrained and then imbibed from both sides with the imbibing dispersion. Excess imbibing dispersion was carefully removed from the surfaces of the microporous polymer scaffold by wiping with a lint-free cloth. The microporous polymer scaffold was then dried with a heat gun set to 100°C until visibly dry (up to about 1 minute),

and then heat treated in a hot air convection oven at 115°C for an additional hour. The resulting electrolyzer porous diaphragm had the properties described in Table 2.

[000219] **[Example 10]**

[000220] An ultrahigh molecular weight PE microporous polymer scaffold was made using a gel process. The resulting microporous polymer scaffold "G" had the properties described in Table 1.

[000221] A substantially aqueous imbibing dispersion was prepared comprising yttria-stabilized zirconia nanoparticles (ZRYS3 available from Nyacol Nano Technologies, Inc.). The nanoparticles are nominally 3 mol% yttria, 32 nanometers in diameter, and the as-received dispersion is 52 mass% in water. To the as-received dispersion, 2 mass% 1-hexanol and 2 mass% Tergitol TMN-10 were added, and the mixture was agitated to emulsify the 1-hexanol. A layer of microporous polymer scaffold was restrained and then imbibed from both sides with the imbibing dispersion. Excess imbibing dispersion was carefully removed from the surfaces of the microporous polymer scaffold by wiping with a lint-free cloth. The microporous polymer scaffold was then dried with a heat gun set to 100°C until visibly dry (up to about 1 minute), and then heat treated in a hot air convection oven at 115°C for an additional hour. The resulting electrolyzer porous diaphragm had the properties described in Table 2.

[000222] **[Example 11]**

[000223] An ultrahigh molecular weight PE microporous polymer scaffold was made using a gel process in a similar manner to Example 10. The resulting microporous polymer scaffold "G" had the properties described in Table 1.

[000224] A substantially aqueous imbibing dispersion was prepared comprising yttria-stabilized zirconia nanoparticles (ZRYS3 available from Nyacol Nano Technologies, Inc.). The nanoparticles are nominally 3 mol% yttria, 32 nanometers in diameter, and the as-received dispersion is 52 mass% in water. To the as-received dispersion, 2 mass% 1-hexanol and 2 mass% Tergitol TMN-10 were added, and the mixture was agitated to emulsify the 1-hexanol. 2 layers of microporous polymer scaffold was restrained and then imbibed from both sides with the imbibing dispersion. Excess imbibing dispersion was carefully removed from the surfaces of the microporous polymer scaffold by wiping with a lint-free cloth. The microporous polymer scaffolds were then dried with a heat gun set to 100°C until visibly dry (up to about 1 minute), leading the dispersion to create a bond between the layers, and then heat treated in a hot air convection oven at 115°C for an additional hour. The resulting electrolyzer porous diaphragm had the properties described in Table 2.

[000225] **[Example 12]**

[000226] An ultrahigh molecular weight PE microporous polymer scaffold was made using a gel process. The resulting microporous polymer scaffold "H" had the properties described in Table 1.

[000227] A substantially aqueous imbibing dispersion was prepared comprising yttria-stabilized zirconia nanoparticles (ZRYS3 available from Nyacol Nano Technologies, Inc.). The nanoparticles are nominally 3 mol% yttria, 32 nanometers in diameter, and the as-received dispersion is 52 mass% in water. To the as-received dispersion, 2 mass% 1-hexanol and 2 mass% Tergitol TMN-10 were added, and the mixture was agitated to emulsify the 1-hexanol. A layer of microporous polymer scaffold was restrained and then imbibed from both sides with the imbibing dispersion. Excess imbibing dispersion was carefully removed from the surfaces of the microporous polymer scaffold by wiping with a lint-free cloth. The microporous polymer scaffold was then dried with a heat gun set to 100°C until visibly dry (up to about 1 minute), and then heat treated in a hot air convection oven at 115°C for an additional hour. The resulting electrolyzer porous diaphragm had the properties described in Table 2.

[000228] **[Example 13]**

[000229] An ultrahigh molecular weight PE microporous polymer scaffold was made using a gel process. The resulting microporous polymer scaffold "H" had the properties described in Table 1.

[000230] A substantially aqueous imbibing dispersion was prepared comprising yttria-stabilized zirconia nanoparticles (ZRYS3 available from Nyacol Nano Technologies, Inc.). The nanoparticles are nominally 3 mol% yttria, 32 nanometers in diameter, and the as-received dispersion is 52 mass% in water. To the as-received dispersion, 2 mass% 1-hexanol and 2 mass% Tergitol TMN-10 were added, and the mixture was agitated to emulsify the 1-hexanol. 2 layers of microporous polymer scaffold was restrained and then imbibed from both sides with the imbibing dispersion. Excess imbibing dispersion was carefully removed from the surfaces of the microporous polymer scaffold by wiping with a lint-free cloth. The microporous polymer scaffolds were then dried with a heat gun set to 100°C until visibly dry (up to about 1 minute), leading the dispersion to create a bond between the layers, and then heat treated in a hot air convection oven at 115°C for an additional hour. The resulting electrolyzer porous diaphragm had the properties described in Table 2.

[000231] **[Example 14]**

[000232] An expanded functional copolymer based on the teaching of US8658707B, polymer B in example 23 of US8658707B, comprising the copolymer of TFE and PSVE was paste processed and expanded based on those teachings. The resulting microporous polymer scaffold "C" had the properties described in Table 1.

[000233] A substantially aqueous imbibing dispersion was prepared comprising yttria-stabilized zirconia nanoparticles (ZRYS3 available from Nyacol Nano Technologies, Inc.). The nanoparticles are nominally 3 mol% yttria, 32 nanometers in diameter, and the as-received dispersion is 52 mass% in water. To the as-received dispersion, 2 mass% 1-hexanol and 2 mass% Tergitol TMN-10 were added, and the mixture was agitated to emulsify the 1-hexanol. A layer of microporous polymer scaffold was restrained and then imbibed from both sides with the imbibing dispersion. Excess imbibing dispersion was carefully removed from the surfaces of the microporous polymer scaffold by wiping with a lint-free cloth. The microporous polymer scaffold was then dried with a heat gun set to 125°C until visibly dry (up to about 1 minute), and then heat treated in a hot air convection oven at 150°C for an additional hour. The resulting electrolyzer porous diaphragm had the properties described in Table 2.

[000234] **[Example 15]**

[000235] An expanded functional copolymer based on the teaching of US8658707B, polymer B in example 23 of US8658707B, comprising the copolymer of TFE and PSVE was paste processed and expanded based on those teachings. The resulting microporous polymer scaffold “D” had the properties described in Table 1.

[000236] A substantially aqueous imbibing dispersion was prepared comprising yttria-stabilized zirconia nanoparticles (ZRYS3 available from Nyacol Nano Technologies, Inc.). The nanoparticles are nominally 3 mol% yttria, 32 nanometers in diameter, and the as-received dispersion is 52 mass% in water. To the as-received dispersion, 2 mass% 1-hexanol and 2 mass% Tergitol TMN-10 were added, and the mixture was agitated to emulsify the 1-hexanol. A layer of microporous polymer scaffold was restrained and then imbibed from both sides with the imbibing dispersion. Excess imbibing dispersion was carefully removed from the surfaces of the microporous polymer scaffold by wiping with a lint-free cloth. The microporous polymer scaffold was then dried with a heat gun set to 125°C until visibly dry (up to about 1 minute), and then heat treated in a hot air convection oven at 150°C for an additional hour. The resulting electrolyzer porous diaphragm had the properties described in Table 2.

[000237] **[Example 16]**

[000238] An expanded functional copolymer microporous scaffold was produced as described in Example 15. The resulting microporous polymer scaffold “D” had the properties described in Table 1.

[000239] A substantially aqueous imbibing dispersion was prepared comprising yttria-stabilized zirconia nanoparticles (ZRYS3 available from Nyacol Nano Technologies, Inc.). The nanoparticles are nominally 3 mol% yttria, 32 nanometers in diameter, and the as-received dispersion is 52

mass% in water. To the as-received dispersion, 2 mass% 1-hexanol and 2 mass% Tergitol TMN-10 were added, and the mixture was agitated to emulsify the 1-hexanol. Two layers of microporous polymer scaffold was restrained and then imbibed from both sides with the imbibing dispersion. Excess imbibing dispersion was carefully removed from the surfaces of the microporous polymer scaffold by wiping with a lint-free cloth. The microporous polymer scaffolds were then dried with a heat gun set to 125°C until visibly dry (up to about 1 minute), leading the dispersion to create a bond between the layers, and then heat treated in a hot air convection oven at 150°C for an additional hour. The resulting electrolyzer porous diaphragm had the properties described in Table 2.

[000240] **[Example 17]**

[000241] An expanded functional copolymer based on the teaching of US8658707B, polymer B in example 23 of US8658707B , comprising the copolymer of TFE and PSVE was paste processed and expanded based on those teachings. The resulting microporous polymer scaffold "E" had the properties described in Table 1.

[000242] A substantially aqueous imbibing dispersion was prepared comprising yttria-stabilized zirconia nanoparticles (ZRYS3 available from Nyacol Nano Technologies, Inc.). The nanoparticles are nominally 3 mol% yttria, 32 nanometers in diameter, and the as-received dispersion is 52 mass% in water. To the as-received dispersion, 2 mass% 1-hexanol and 2 mass% Tergitol TMN-10 were added, and the mixture was agitated to emulsify the 1-hexanol. A layer of microporous polymer scaffold was restrained and then imbibed from both sides with the imbibing dispersion. Excess imbibing dispersion was carefully removed from the surfaces of the microporous polymer scaffold by wiping with a lint-free cloth. The microporous polymer scaffold was then dried with a heat gun set to 125°C until visibly dry (up to about 1 minute), and then heat treated in a hot air convection oven at 150°C for an additional hour. The resulting electrolyzer porous diaphragm had the properties described in Table 2.

[000243] **[Example 18]**

[000244] An expanded functional copolymer microporous scaffold was prepared as described in Example 17. The resulting microporous polymer scaffold "E" had the properties described in Table 1.

[000245] A substantially aqueous imbibing dispersion was prepared comprising yttria-stabilized zirconia nanoparticles (ZRYS3 available from Nyacol Nano Technologies, Inc.). The nanoparticles are nominally 3 mol% yttria, 32 nanometers in diameter, and the as-received dispersion is 52 mass% in water. The as-received dispersion was diluted with water to 34.3 mass% solids, and to this diluted dispersion, 2 mass% 1-hexanol and 2 mass% Tergitol TMN-10 were added, and

the mixture was agitated to emulsify the 1-hexanol. A layer of microporous polymer scaffold was restrained and then imbibed from both sides with the imbibing dispersion. Excess imbibing dispersion was carefully removed from the surfaces of the microporous polymer scaffold by wiping with a lint-free cloth. The microporous polymer scaffold was then dried with a heat gun set to 125°C until visibly dry (up to about 1 minute), and then heat treated in a hot air convection oven at 150°C for an additional hour. The resulting electrolyzer porous diaphragm had the properties described in Table 2.

[000246] **[Example 19]**

[000247] An expanded functional copolymer microporous scaffold was prepared as described in Example 17. The resulting microporous polymer scaffold "E" had the properties described in Table 1.

[000248] A substantially aqueous imbibing dispersion was prepared comprising yttria-stabilized zirconia nanoparticles (ZRYS3 available from Nyacol Nano Technologies, Inc.). The nanoparticles are nominally 3 mol% yttria, 32 nanometers in diameter, and the as-received dispersion is 52 mass% in water. The as-received dispersion was diluted with water to 34.3 mass% solids, and to this diluted dispersion, 2 mass% 1-hexanol and 2 mass% Tergitol TMN-10 were added, and the mixture was agitated to emulsify the 1-hexanol. A layer of microporous polymer scaffold was restrained and then imbibed from both sides with the imbibing dispersion. Excess imbibing dispersion was carefully removed from the surfaces of the microporous polymer scaffold by wiping with a lint-free cloth. The microporous polymer scaffold was then dried with a heat gun set to 125°C until visibly dry (up to about 1 minute), and then heat treated in a hot air convection oven at 150°C for an additional hour. The resulting electrolyzer porous diaphragm had the properties described in Table 2.

[000249] **[Comparative Example 1]**

[000250] A scaffold composed of an open mesh polyphenylene sulfide fabric which is symmetrically coated with a mixture of a polymer and zirconium oxide (ZIRFON PERL UTP 500), available from AGFA, having a thickness of about 500 µm, was used as a comparative example. The scaffold had an ex-situ ionic resistance of 4.150 Ohms.

[000251] As can be seen from Table 2, the electrolyzer porous diaphragms of Examples 1-19 have much lower ionic resistance than the scaffold of Comparative Example 1, demonstrating their improved utility in e.g., liquid alkaline water electrolysis. As can also be seen from Tables 1 and 2, the electrolyzer porous diaphragms of Examples 1-19 have acceptable strength properties to function effectively in liquid alkaline water electrolysis.

Table 1: Properties of microporous polymer scaffolds of the Examples

Microporous polymer scaffold type	Mass-per-area (g/m^2)	Non-contact thickness (μm)	Porosity (vol%)	Bubble point (bar)	Volume Specific Surface Area (m^2/cc)	Area Specific Surface area $m^2_{surface}/m^2$	MD ATS (N/mm)	TD ATS (N/mm)	Geometric mean ATS (N/mm)	Geometric mean ATS/ diaphragm contact thickness (MPa)	ATS (2^{nd} direction)/ diaphragm contact thickness (MPa)	MD MTS (MPa)	TD MTS (MPa)	Geometric mean MTS (MPa)	Strength balance ratio (second/first directions)
A	37.0	70	76.0	5.3	37.9	636	5.407	6.514	5.935	156.2	142.4	321.5	387.4	352.9	0.8
B	4.4	23	90.9	3.4	42.9	86	0.713	0.531	0.615	61.5	53.1	348.5	259.4	300.7	0.7
C	19.9	145	93.8	1.2	15.0	135	1.453	0.928	1.161	14.2	11.3	160.7	102.6	128.4	0.6
D	24.9	23	51.8	1.3	11.4	129	1.403	1.468	1.435	71.7	70.2	124.1	129.9	127.0	1.0
E	28.3	43	69.8	1.6	14.8	190	1.345	1.354	1.349	33.7	33.6	117.8	137.3	127.2	1.0
F	15.0	108	85.4	3.2	15.6	246	2.241	2.241	2.241	36.1	36.1	140.4	140.4	140.4	1.0
G	3.1	19	83.4	1.4	15.7	51	0.331	0.432	0.378	16.4	14.4	101.5	132.7	116.0	0.8
H	3.5	17	77.9	2.1	18.8	70	0.341	0.676	0.480	20.0	14.2	91.0	180.1	128.0	0.5
I	11.6	34	84.7	3.3	36.3	191	1.870	0.946	1.330	88.6	63.1	355.9	180.0	253.1	0.5

MD refers to machine direction; TD refers to transverse direction; the lower value of the MD and TD corresponds to the second direction

ATS refers to absolute tensile strength and MTS refers to matrix tensile strength

Table 2: Properties of the diaphragms of the Examples

Diaphragm	Microporous polymer scaffold type	Number of microporous polymer scaffold layers	Thickness (µm)	Force to Short (N)	MD ATS (N/mm)	TD ATS (N/mm)	Geometric mean ATS (N/mm)	Diaphragm bubble point (bar)	Ex-situ ionic resistance (Ohm)
Example 1	A	1	38.0	-	5.09	5.90	5.48	-	0.274
Example 2	B	1	10.0	98	0.644	0.715	0.679	11.7	0.102
Example 3	B	2	15.0	93	-	-	-	7.0	0.242
Example 4	B	3	25.0	116	-	-	-	17.8	0.347
Example 5	B	4	30.0	111	2.861	1.990	2.386	20.7	0.451
Example 6	B	8	74.0	302	-	-	-	-	1.290
Example 7	I	1	15.0	-	-	-	-	-	0.398
Example 8	I	2	36.0	-	-	-	-	-	0.394
Example 9	F	1	62.0	62	-	-	-	-	1.430
Example 10	G	1	23.0	76	-	-	-	-	0.360
Example 11	G	2	34.0	80	-	-	-	-	0.618
Example 12	H	1	24.0	71	-	-	-	-	0.572
Example 13	H	2	48.0	67	-	-	-	-	0.968
Example 14	C	1	82.0	267	-	-	-	-	0.972
Example 15	D	1	20.0	49	1.62	1.38	1.50	5.3	0.604
Example 16	D	2	42.0	-	-	-	-	11.5	1.220
Example 17	E	1	40.0	58	1.37	1.32	1.34	10.5	0.355
Example 18	E	1	42.0	53	-	-	-	5.0	0.246
Example 19	E	1	45.0	40	-	-	-	1.1	0.140

[0001] In the scaffolds and electrolyzer porous diaphragms used in the Examples, the minimum MTS (corresponding to the second direction) is always in either the MD or TD.

[0002] As described above, the electrolyzer porous diaphragms of the present disclosure, comprising microporous polymer scaffolds with high MTS, have shown good handleability (e.g., as evidenced by good dimensional stability and successful assembly in liquid alkaline electrolyzers) and good electrical shorting properties (i.e., protection against electrical shorting as demonstrated, for example, by successful operation in liquid alkaline electrolyzers, and by high force-to-short values), despite being extremely thin. It is surprising that high matrix tensile strength, which is a property of the microporous polymer scaffold and that is measured in the "in-plane" direction of the microporous polymer scaffold, has enabled high shorting protection, which is a property of the porous diaphragm and that is measured in the "thickness" direction of the electrolyzer porous diaphragm (which is also the thickness direction of the microporous polymer scaffold). All of the microporous polymer scaffolds of the Examples have MTS in the second direction in excess of 90 MPa as shown in Table 1. The improved electrical shorting properties are evidenced by the high force to short values exhibited by the electrolyzer porous diaphragms of the invention of at least 40 N as shown in Table 2. Thus, high force to short is achieved in cells having the relatively thin electrolyzer porous diaphragms of the invention with thicknesses of 82 μm or lower.

[0003] Figures 1 and 2 show the polarization curves of current density vs average voltage for the scaffold of Comparative Example 1 and each of the diaphragms of Examples 10, 14, 15, 17, 18 and 19. The average voltage for the scaffold of Comparative Example 1 is higher than the electrolyzer porous diaphragms of Examples 10, 14, 15, 17, 18 and 19, for a given current density, further demonstrating the utility of the electrolyzer porous diaphragms of the present disclosure in e.g., alkaline water electrolysis. Moreover, Figure 3 shows the polarization curve slope for the scaffold of Comparative Example 1 and each of the electrolyzer porous diaphragms of Examples 10, 14, 15, 17, 18 and 19. Comparative Example 1 has the highest polarization curve slope, further demonstrating the utility of the electrolyzer porous diaphragms of the present disclosure in e.g., alkaline water electrolysis. Lower average voltage and polarization curve slope values are beneficial over higher values.

[0004] All ranges described herein are exemplary in nature and include any and all values in between. The terms "substantially," "approximately" and "about" used herein are interchangeable and refer to a measurement that includes the stated measurement and any measurements reasonably close to the stated measurement. Measurements that are reasonably close to the stated measurement deviate from the stated measurement by a reasonably small amount as

understood and readily ascertained by individuals having ordinary skill in the relevant arts. Such deviations may be attributable to measurement error, differences in measurement and/or manufacturing equipment calibration, human error in reading and/or setting measurements, minor adjustments made to optimize performance and/or structural parameters in view of differences in measurements associated with other components, particular implementation scenarios, imprecise adjustment and/or manipulation of objects by a person or machine. In the event it is determined that individuals having ordinary skill in the relevant arts would not readily ascertain values for such reasonably small differences, the terms "about" and "approximately" can be understood to mean plus or minus 10% of the stated value.

[0005] Throughout the description and claims, the terms take the meanings explicitly defined herein, unless the context clearly dictates otherwise.

[0006] The phrases "in one embodiment", "in an embodiment" and "in some embodiments" etc. as used herein do not necessarily refer to the same embodiment(s), though they may. Furthermore, the phrases "in another embodiment" and "in some other embodiments" as used herein do not necessarily refer to a different embodiment, though they may. All embodiments of the disclosure are intended to be combinable.

[0007] The terms "comprises" and "comprising" mean to include but not limited to, such that further features may be present. The terms may also mean to consist of.

[0008] All references and test methods cited herein are incorporated by reference in their entireties.

CLAIMS:

1. An electrolyzer porous diaphragm comprising:
   a microporous polymer scaffold having a plurality of pores having inner surfaces, wherein the microporous polymer scaffold has a first direction, a second direction and a thickness direction, wherein the first direction is orthogonal to the second direction, and the first and second directions are each orthogonal to the thickness direction; and
   a hydrophilic additive, wherein the hydrophilic additive is deposited on the inner surfaces of the plurality of pores of the microporous polymer scaffold,
   wherein the microporous polymer scaffold has a matrix tensile strength (MTS) in the second direction of at least about 55 MPa, wherein the second direction is the direction in which the microporous polymer scaffold has its minimum matrix tensile strength, and
   wherein the electrolyzer porous diaphragm has a contact thickness of less than about 150 μm.

2. An electrolyzer porous diaphragm according to Claim 1, wherein the microporous polymer scaffold has a geometric mean MTS of at least about 90 MPa.

3. An electrolyzer porous diaphragm according to Claim 1 or Claim 2, wherein the geometric mean absolute tensile strength of the microporous polymer scaffold/ electrolyzer porous diaphragm contact thickness is at least about 10 MPa.

4. An electrolyzer porous diaphragm according to any one of Claims 1-3, wherein the absolute tensile strength of the microporous polymer scaffold in the second direction / electrolyzer porous diaphragm contact thickness is at least about 8 MPa.

5. An electrolyzer porous diaphragm according to any one of Claims 1-4, wherein the microporous polymer scaffold has a tensile strength balance ratio, which is the absolute tensile strength in the second direction / absolute tensile strength in the first direction, in the range of from 0.45 to 1.

6. An electrolyzer porous diaphragm according to any preceding Claim, wherein the microporous polymer scaffold has a mass-per-area ranging from about 1 g/m^2 to about 60 g/m^2.

7. An electrolyzer porous diaphragm according to any preceding Claim, wherein the microporous polymer scaffold has a porosity of at least about 40 vol% or at least about 75 vol%.

8. An electrolyzer porous diaphragm according to any preceding Claim, wherein the electrolyzer porous diaphragm has a contact thickness ranging from about 2 μm to about 75 μm.

9. An electrolyzer porous diaphragm according to any preceding Claim, wherein the microporous polymer scaffold has a bubble point pressure of at least about 1 bar.

10. An electrolyzer porous diaphragm according to any preceding Claim, wherein the electrolyzer porous diaphragm comprises one or more microporous polymer scaffolds.

11. An electrolyzer porous diaphragm according to any preceding Claim, wherein the microporous polymer scaffold is formed from any one selected from a non-fluorinated polymer, a partially fluorinated polymer, a perfluorinated polymer, and any combination thereof.

12. An electrolyzer porous diaphragm according to Claim 11, wherein the microporous polymer scaffold is formed from a polytetrafluoroethylene (PTFE), a polyethylene (PE), a polypropylene (PP) or copolymer thereof.

13. An electrolyzer porous diaphragm according to Claim 12, wherein the microporous polymer scaffold is formed from expanded PTFE (ePTFE) or expanded PE (ePE).

14. An electrolyzer porous diaphragm according to any preceding Claim, wherein the microporous polymer scaffold has a microstructure comprising nodes, fibrils and the plurality of scaffold pores, wherein the nodes are interconnected by the fibrils, and the plurality of scaffold pores are void spaces between the nodes and fibrils.

15. An electrolyzer porous diaphragm according to Claim 14, wherein the hydrophilic additive is deposited on the surfaces of the nodes and fibrils of the microporous polymer scaffold without occluding the scaffold pores.

16. An electrolyzer porous diaphragm according to Claim 14 or Claim 15, wherein the hydrophilic additive is deposited on the surfaces of the nodes and fibrils throughout a thickness of the microporous polymer scaffold.

17. An electrolyzer porous diaphragm according to any preceding Claim, wherein the microporous polymer scaffold has a first surface and a second surface opposite the first surface, and wherein the hydrophilic additive is deposited on the first surface of the microporous polymer scaffold and/or the second surface of the microporous polymer scaffold.

18. An electrolyzer porous diaphragm according to any preceding Claim, wherein the electrolyzer porous diaphragm contains from about 2 wt% to about 95 wt% of the hydrophilic additive, wherein the total weight of the electrolyzer porous diaphragm is 100 wt%.

19. An electrolyzer porous diaphragm according to any preceding Claim, wherein the hydrophilic additive comprises a polymer or ceramic.

20. An electrolyzer porous diaphragm according to Claim 19, wherein the polymer is an ionomer selected from any one of an anion exchange ionomer, a cation exchange ionomer, and a combination thereof, wherein the ionomer is perfluorinated, partially fluorinated or non-fluorinated;
or wherein the polymer is a non-ionic polymer.

21. An electrolyzer porous diaphragm according to Claim 20, wherein the ionomer is a perfluorosulfonic acid or a salt of a perfluorosulfonic acid.

22. An electrolyzer porous diaphragm according to Claim 19, wherein the ceramic is selected from any one of silica, alumina, titania, ceria, zirconia, yttria-stabilized zirconia, and a combination thereof.

23. An electrolyzer porous diaphragm according to any preceding Claim, wherein the hydrophilic additive is deposited on the inner surfaces of the plurality of pores of the microporous polymer scaffold by imbibing the microporous polymer scaffold with an imbibing fluid, wherein the imbibing fluid comprises the hydrophilic additive and a liquid carrier, and drying the microporous polymer scaffold imbibed with the imbibing fluid.

24. An electrolyzer porous diaphragm according to Claim 23, wherein the liquid carrier is any one selected from water, a C1-C5 alcohol, and any combination thereof.

25. An electrolyzer porous diaphragm according to Claim 24, wherein the C1-C5 alcohol is any one selected from methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol and pentan-1-ol.

26. An electrolyzer porous diaphragm according to any one of Claims 23-25, wherein the imbibing fluid is prepared by dissolving or mixing the hydrophilic additive in the liquid carrier.

27. An electrolyzer porous diaphragm according to any preceding Claim, wherein the electrolyzer porous diaphragm is for liquid alkaline water electrolysis.

28. An electrolyzer porous diaphragm comprising:
a microporous polymer scaffold having a plurality of pores having inner surfaces; and
a hydrophilic additive, wherein the hydrophilic additive is deposited on the inner surfaces of the plurality of pores of the microporous polymer scaffold,
wherein the electrolyzer porous diaphragm has a first direction, a second direction and a thickness direction, wherein the first direction is orthogonal to the second direction, and the first and second directions are each orthogonal to the thickness direction,
wherein the electrolyzer porous diaphragm has an absolute tensile strength in the second direction / electrolyzer porous diaphragm contact thickness of at least about 8 MPa, wherein the second direction is the direction in which the electrolyzer porous diaphragm has its minimum absolute tensile strength, and
wherein the electrolyzer porous diaphragm has a contact thickness of less than about 150 μm.

29. A method of producing an electrolyzer porous diaphragm as defined in any of Claims 1-28, the method comprising:
imbibing the microporous polymer scaffold with an imbibing fluid, wherein the imbibing fluid comprises the hydrophilic additive and a liquid carrier; and
drying the microporous polymer scaffold imbibed with the imbibing fluid.

30. A method according to Claim 29, wherein the liquid carrier is any one selected from water, a C1-C5 alcohol, and any combination thereof.

31. A method according to Claim 30, wherein the C1-C5 alcohol is any one selected from methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol and pentan-1-ol.

32. A method according to any one of Claims 29-31, further comprising preparing the imbibing fluid by dissolving or mixing the hydrophilic additive in the liquid carrier.

33. An electrolyzer comprising: an anode; a cathode; the porous diaphragm as defined in any of Claims 1-28; and a liquid electrolyte, wherein the electrolyzer porous diaphragm is positioned between the anode and the cathode, and wherein the liquid electrolyte at least partially wets the electrolyzer porous diaphragm.

34. An electrolyzer according to Claim 33, wherein the anode comprises any one selected from nickel, cobalt and iron.

35. An electrolyzer according to Claim 33 or Claim 34, wherein the cathode comprises any one selected from nickel, platinum and carbon.

36. An electrolyzer according to any one of Claims 33-35, wherein the liquid electrolyte is a liquid alkaline electrolyte, optionally wherein the liquid alkaline electrolyte is an aqueous or substantially aqueous alkaline solution.

37. An electrolyzer according to Claim 36, wherein the liquid alkaline electrolyte comprises a metal hydroxide.

38. An electrolyzer according to Claim 37, wherein the metal hydroxide is sodium hydroxide or potassium hydroxide.

39. Use of the electrolyzer porous diaphragm as defined in any one of Claims 1-28 or the electrolyzer as defined in any of Claims 33-38 in the electrolysis of water to produce hydrogen.

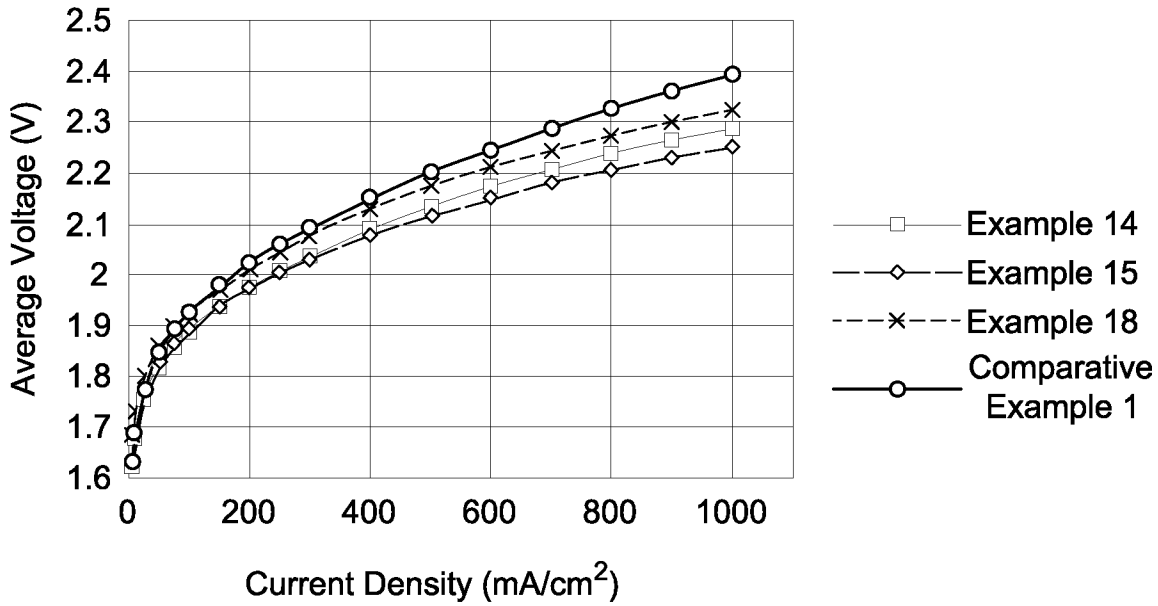

Average Voltage (V)
2.5
2.4
2.3
2.2
2.1
2
1.9
1.8
1.7
1.6
0
200
400
600
800
1000
Current Density (mA/cm2)
Example 14
Example 15
Example 18
Comparative Example 1

Fig. 1

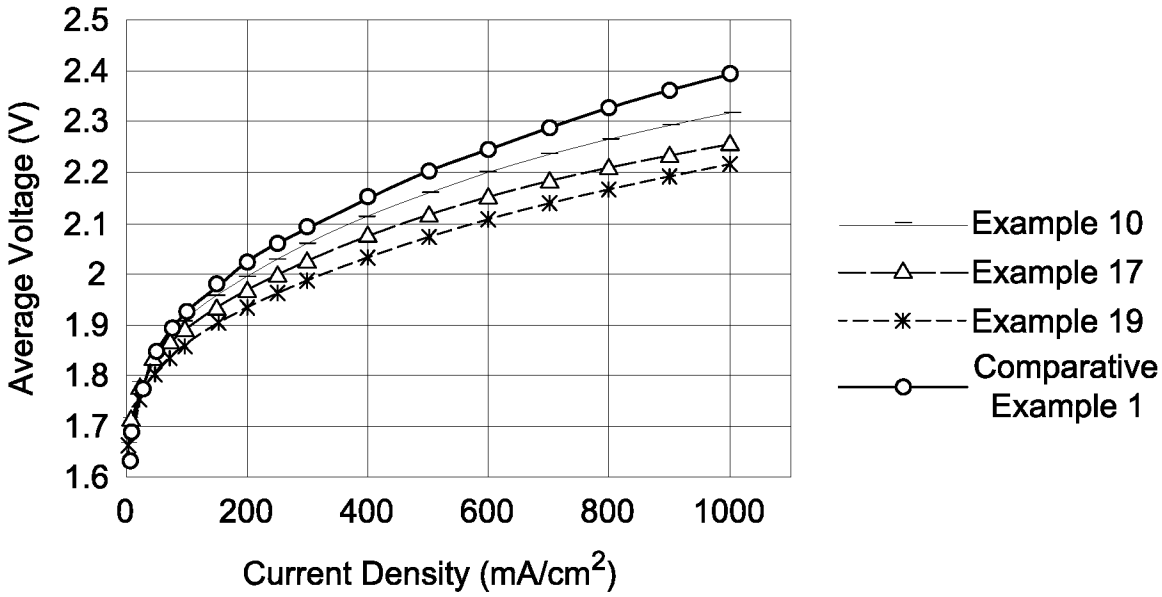

Average Voltage (V)
2.5
2.4
2.3
2.2
2.1
2
1.9
1.8
1.7
1.6
0
200
400
600
800
1000
Current Density (mA/cm2)
Example 10
Example 17
Example 19
Comparative Example 1

Fig. 2

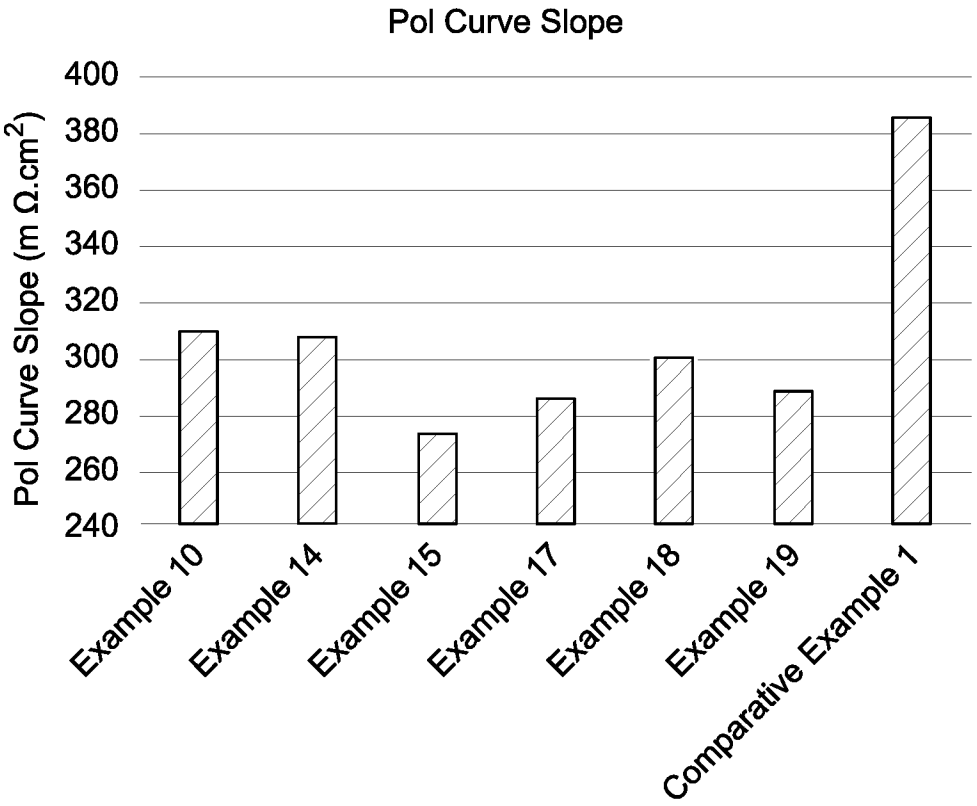

Pol Curve Slope
Pol Curve Slope (m Ω.cm2)
400
380
360
340
320
300
280
260
240
Example 10
Example 14
Example 15
Example 17
Example 18
Example 19
Comparative Example 1

Fig. 3

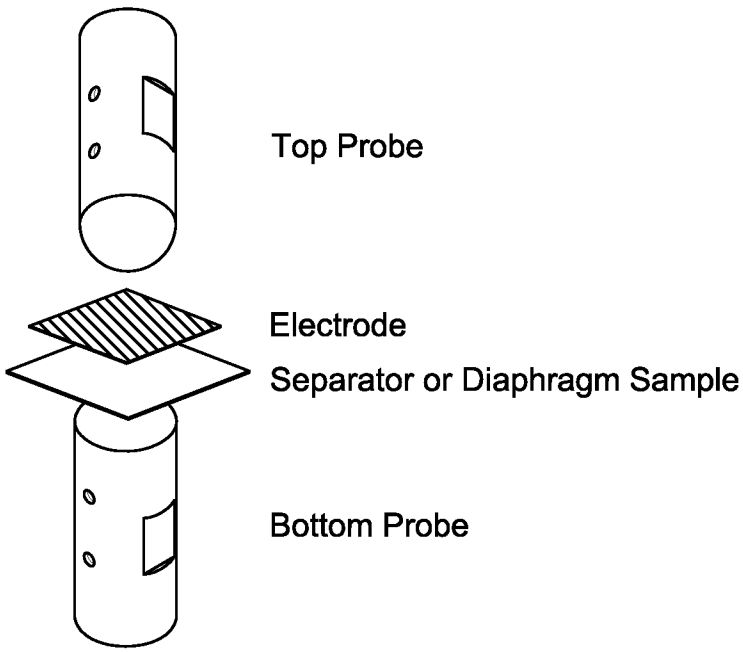

Top Probe
Electrode
Separator or Diaphragm Sample
Bottom Probe

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/035990

A. CLASSIFICATION OF SUBJECT MATTER

INV. C25B1/04 C25B9/19 C25B13/02 C25B13/07 C25B13/08
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C25B

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP H10 92444 A (JAPAN GORE TEX INC) 10 April 1998 (1998-04-10) the whole document -----	1-35,39
X	US 2014/332403 A1 (CARRILERO BORBUJO ISABEL [ES] ET AL) 13 November 2014 (2014-11-13) abstract; claims 15-27; example 1 paragraph [0037] - paragraph [0083]; figures 1-4 -----	1-23, 26-29, 32-39

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 October 2024	16/10/2024

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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