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(54) **HEAT AND MOISTURE EXCHANGE DEVICE**

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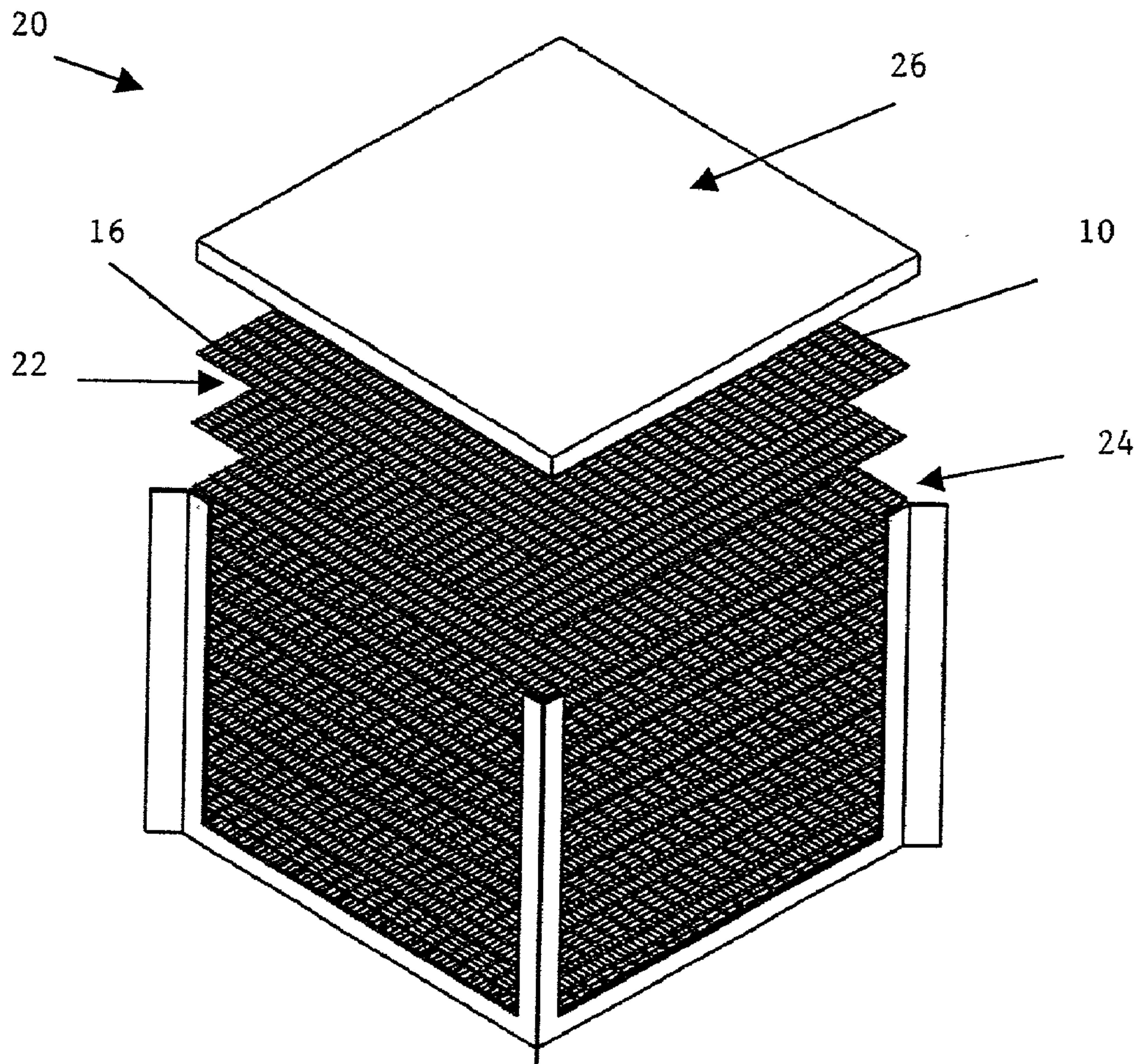
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**Related U.S. Application Data**

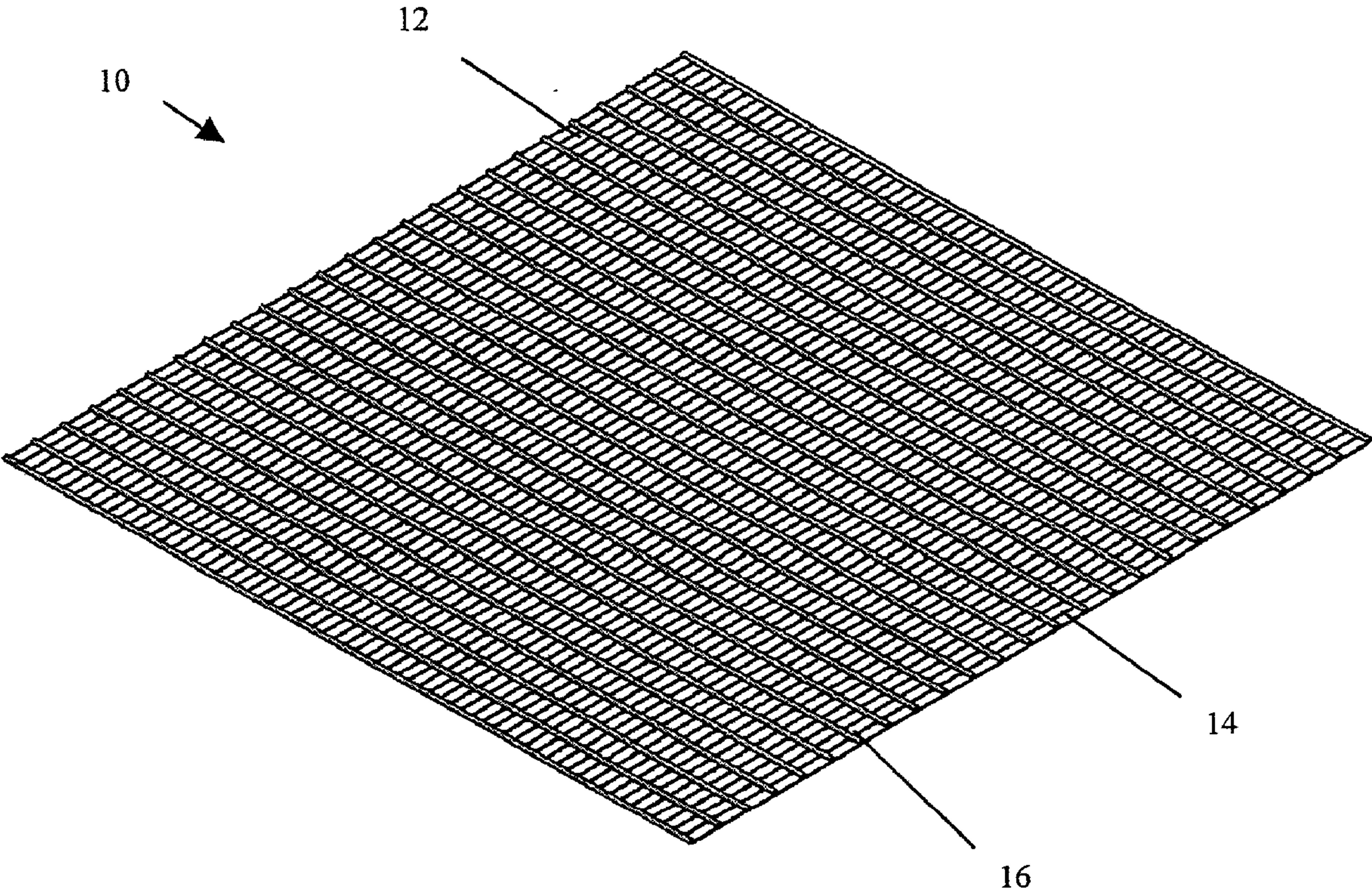
(60) Provisional application No. 60/275,459, filed on Mar.  
13, 2001. Provisional application No. 60/327,746,  
filed on Oct. 9, 2001, now abandoned.

(57) **ABSTRACT**

A unitary humidity exchange cell (HUX) is disclosed that includes at least one composite membrane, disposed between at least one first chamber for flow of the first fluid therethrough and at least one second chamber for flow of the second fluid therethrough. The composite membrane include an at least partially sulfonated humidity-conducting polymer comprising residues derived from at least one arylvinyl monomer; and a reinforcing substrate bonded thereto. The product finds utility in a variety of physical and chemical processes and products whereby moisture or other highly polar liquid or gas transfer, exchange removal or delivery is important. A notable application is the Membrane Energy Recovery Ventilator (MERV) in which both heat and moisture is transferred between two air streams, one intake and one exhaust, from an air-conditioned building.







**FIG. 1**

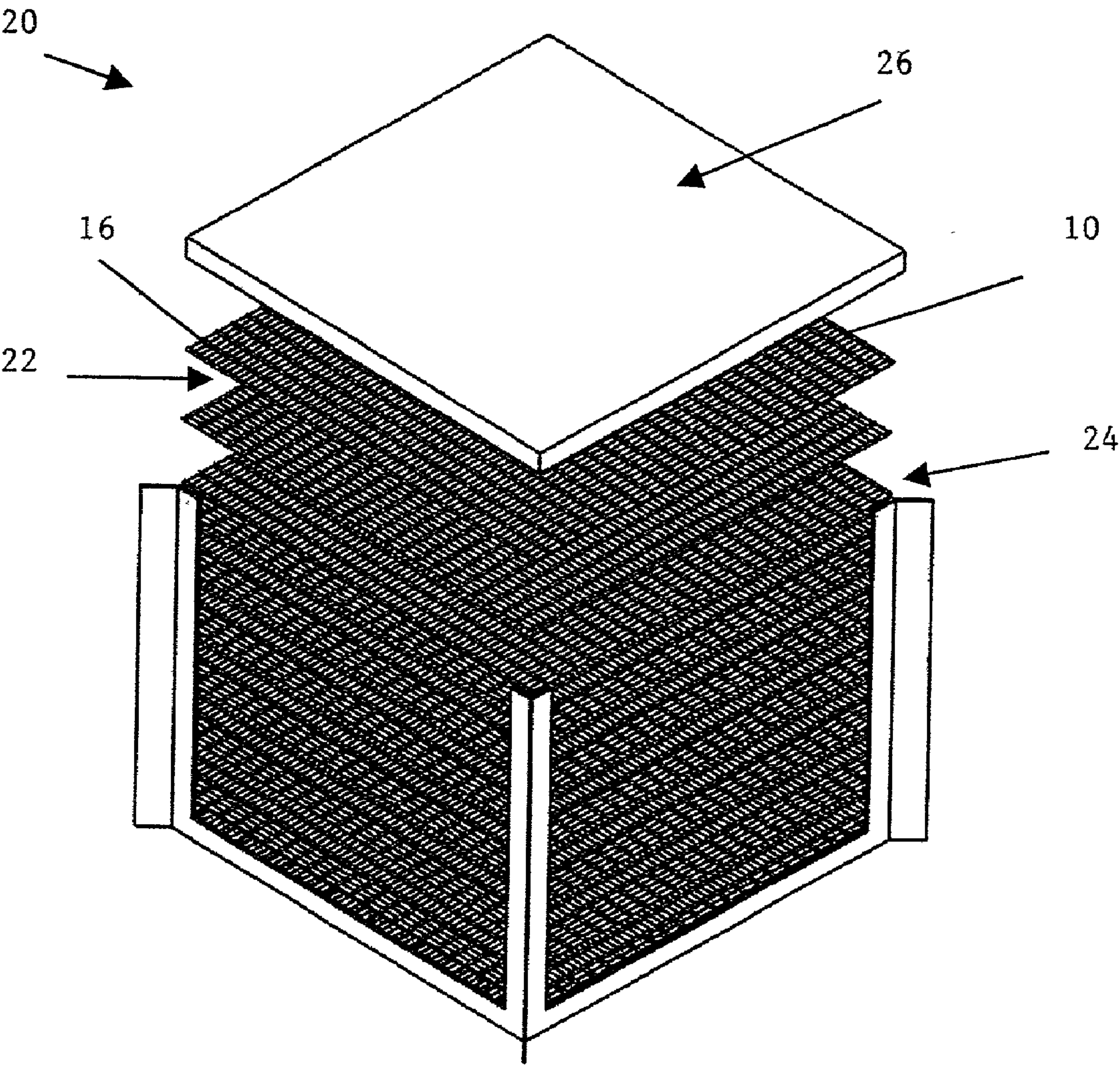


FIG. 2



## HEAT AND MOISTURE EXCHANGE DEVICE

### CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority from U.S. Provisional applications 60/275,459, filed Mar. 13, 2001, and 60/327,746, filed Oct. 9, 2001.

### FIELD OF THE INVENTION

[0002] The invention relates to devices and apparatus for transfer of heat and water between fluids, via a composite polymer membrane.

### BACKGROUND OF THE INVENTION

[0003] A unitary humidity exchange cell (or HUX), as the name implies, is an element of a device that is capable of transferring water or other highly polar liquid or gas from one side of the cell to the other by action of a difference in some quantity or gradient across said cell. A key operational characteristic of the HUX cell is that a difference of some intensive or extensive property of the system (relative to the surrounding) leads to a gradient change of said property to effect mass transfer of water or some other highly polar liquid or gas from one side of the membrane to the other with or without an accompanying flow of electrons, protons, ions or molecules other than said water or other highly polar liquid or gas. It is under the influence of this property that exchange in liquid water or some other highly polar liquid or gas occurs across the permaselective membrane. This transfer of water or some other highly polar liquid or gas may or may not be accompanied by evaporation of said water or other highly polar liquid or gas into (or from) the stream by the absorption of heat or adiabatically or by some other thermodynamic means; for example the condensation or evaporation of liquid water or some other highly polar liquid or gas or the simple diffusion of water or some other highly polar liquid or gas into a pure liquid stream. A finite gradient across the membrane must exist in some quantity; examples are vapor pressure, osmotic or hydrostatic pressure, chemical, thermochemical, electrochemical, magnetochemical potential, as well as thermal (temperature or heat content), electric, electromagnetic, thermoelectric, or electrothermal potential difference. There must be at least two streams, one supplied to each surface of said membrane by some means either as a liquid or vapor flow each of which differs in at least one identical property of the system. The system attempts to reach a thermodynamic equilibrium by transporting water or some other highly polar liquid or gas from one stream to the other. The orientation of the streams to one another is considered arbitrary for the invention; these may be counter flow, coflow, crossflow, mixed flow or any other geometric arrangement of one or more streams. Water or some other highly polar liquid or gas transport (e.g. hydrodynamic, electrohydrodynamic, magnetohydrodynamic, diffusion, migration, or convection) occurs until the imposed gradient can no longer meet the physicochemical constraints of the system required to sustain the motion. In many cases, the exchange of water or some other highly polar liquid or gas between the streams is slow, but this may be due to some other limiting factor, such as, boundary layer effects, concentration polarization, hydrostatic pressure lag or gravity, surface tension effects, and convective or frictional effects. However, once these engineering design or system effects are minimized, inevitably, the exchange or transport of water or some other highly polar liquid or gas

is rate-limiting if the permeability of the membrane to water or some other highly polar liquid or gas is poor. Hence, an important object of the invention is that hydrophilic polymer membrane has high permeability to water or some other highly polar liquid or gas; more than necessary for most applications. The hydrophilic polymer membrane (or formulation) must be mechanically supported and there must be means to supply the two streams to said surfaces. A second object of the invention is that the three sub-elements be fabricated as one unit by conventional means at low cost. This requires that the hydrophilic polymer wet the support, achieve intimate contact and demonstrate exceptional adhesion to it. Therefore, a third object of the invention is that the support be a polyolefin or blend thereof such that one component of said hydrophilic polymer is similar in chemical structure to one component of the support.

[0004] HUX cell design is general in that water (liquid or vapor) or other highly polar material (liquid or vapor) can be transferred between any two fluids. Examples of applications are per-vaporation, humidification and dehumidification of fuel cell streams in stacks and devices, drying gases at pressure, tertiary oil recovery, process control for chemical manufacture of chemicals for which water is a reactant, isolation of minerals from mining fluids, industrial separation of oil-water emulsions, microfiltration and ultrafiltration of colloidal suspensions and biological or organic macromolecules for purification, maintaining water content of methanol in direct methanol fuel cells, reverse osmosis for isolation of fresh water from brine, electrolysis cells, dialysis, electro-dialysis, piezo-dialysis, electro-osmosis and chloro-alkali cells.

### SUMMARY OF THE INVENTION

[0005] The present invention relates to cells for transferring heat and moisture between a first fluid and a second fluid. Such a cell comprises at least one composite membrane, disposed between at least one first chamber for flow of the first fluid therethrough and at least one second chamber for flow of the second fluid therethrough; whereby heat and moisture is transferable between the first fluid and second fluid via the composite membrane. The composite membrane may comprise an at least partially sulfonated humidity-conducting polymer comprising residues derived from at least one arylvinyl monomer; and a reinforcing substrate bonded thereto. The cell may additionally include at least one spacer disposed on a surface of the composite membrane. The spacer(s) may have a dimension normal to the surface of the composite membrane corresponding to a height of the first chamber; the longitudinal axis of the at least one spacer may be oriented parallel to a direction of flow of the first fluid in the first chamber. The direction of flow of the first fluid in the first chamber may be orthogonal to a direction of flow of the second fluid in the second chamber, or it may be opposite to it. In some embodiments, a plurality of synthetic polymer ribs are used as spacers; in others, the spacer is merely a bead of an adhesive composition; in still others, the spacer is a corrugated sheet composed of paper or plastic. The invention also relates to cell containing a plurality of composite membranes, and a plurality of alternating first chambers and second chambers, each separated by a composite membrane. The reinforcing substrate of the composite membrane may be a nonwoven fabric, composed of synthetic fibers, particularly one or more polyolefins. The humidity-conducting polymer of the composite membrane may include an additive selected from the group of antioxidants, biocides, flame retardants, uv



stabilizers, hydrophilic plasticizers, and mixtures thereof, particularly, antioxidant(s), biocide(s), and flame retardant(s). The humidity-conducting polymer may be crosslinked using a peroxide initiator and an organometallic enolate coupling agent, particularly, 1,1-di-(tert-butylperoxy)-3,3,5-trimethylcyclohexane and aluminum acetoacetate, or 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3 and aluminum acetoacetate.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0006] FIG. 1 shows a composite membrane for use in a humidity exchange cell according to present invention.

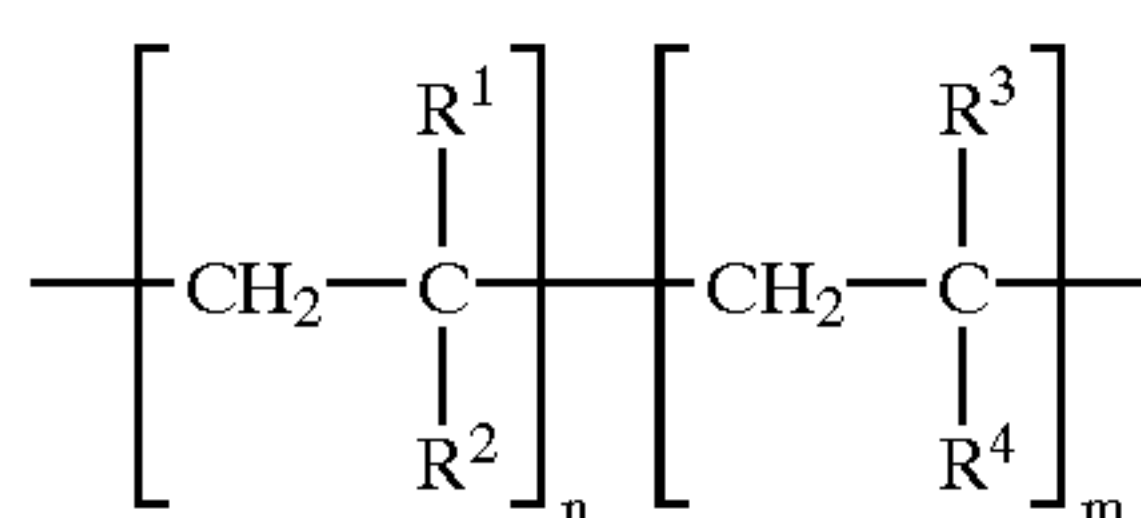
[0007] FIG. 2 is a partially exploded view of a humidity exchange cell according to the present invention.

[0008] FIG. 3 is a graph showing high heat and water transfer using a humidity exchange cell according to the present invention.

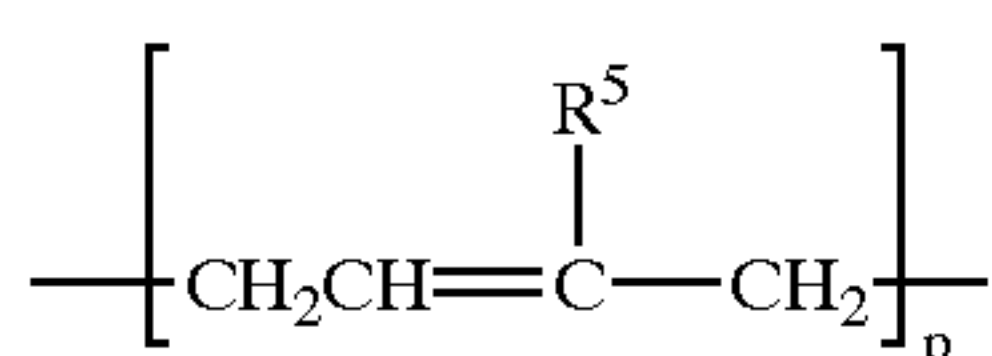
#### DETAILED DESCRIPTION OF THE INVENTION

[0009] FIG. 1 shows a single composite membrane 10 for use in a humidity exchange cell according to the present invention. The membrane includes a continuous film of a humidity-conducting polymer 12 bonded to a reinforcing substrate 14 in the form of a cross-laid mesh or netting. Reinforcing substrate 14 strengthens the membrane so it can be handled, and allows the membrane to withstand pressure differentials without deflecting. As shown in FIG. 1, there are spacers, ribs or ridges 16 adhered to the surface of membrane 10 and running in one direction. The other side of the membrane is a smooth surface of humidity-conducting polymer 12. The height of spacer 16 sets the layer-to-layer spacing. Air channels in the humidity exchange cell are formed by spacers 16 when they rest against the smooth surface of the membrane that is placed on top of it.

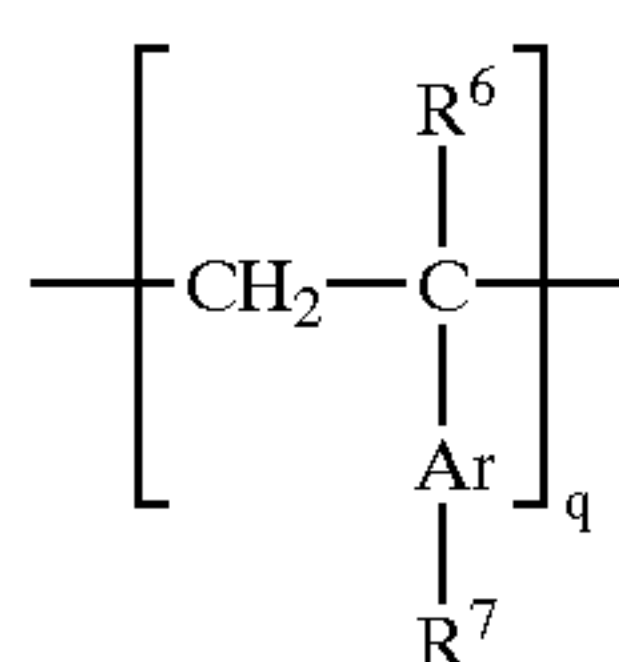
[0010] The humidity-conducting polymer may be an at least partially sulfonated copolymer comprising residues derived from at least one arylvinyl monomer. Accordingly, the polymer includes repeating units of formula III, derived from an arylvinyl monomer, in addition to one or both of the repeating units of formulas I and II, derived from olefin monomers.



I



II



III

[0011] wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup> are chosen independently from the group consisting of hydrogen, nitrile, phenyl and

lower alkyl; R<sup>5</sup> is hydrogen, chlorine or lower alkyl; R<sup>6</sup> is hydrogen or methyl; R<sup>7</sup> is —COOH, —SO<sub>3</sub>H, —P(O)(OR<sup>8</sup>)OH, —R<sup>9</sup>—COOH, —R<sup>9</sup>—SO<sub>3</sub>H, —R<sup>9</sup>—P(O)(OR<sup>8</sup>)OH; R<sup>8</sup> is hydrogen or lower alkyl, R<sup>9</sup> is lower alkylene; Ar is phenyl; and m, n, p, and q are zero or integers from 50 to 10,000.

[0012] The humidity-conducting polymer may be a block, graft or statistical copolymer derived from arylvinyl monomers. Some suitable polymers are described in U.S. Pat. Nos. 5,468,574; 5,679,482; and 6,110,616; the disclosure of each of these is incorporated by reference herein in its entirety. Block and graft copolymers contain relatively long segments made up of a homopolymer derived from one of the comonomers. In contrast, the term “statistical” is used herein to refer to polymers that do not contain long segments made up of homopolymer, and to distinguish these from block and graft copolymers. Preferably, the statistical polymers do not contain more than 15 percent of the total amount of arylvinyl monomer in blocks of arylvinyl monomer of more than 3 units. More preferably, the statistical polymers are not characterized by a high degree of either isotacticity or syndiotacticity. This means that in the carbon-13 NMR spectrum of the statistical polymer the peak areas corresponding to the main chain methylene and methine carbons representing either meso diad sequences or racemic diad sequences should not exceed 75 percent of the total peak area of the main chain methylene and methine carbons.

[0013] A statistical copolymer is a well-defined term of art (see G. Odian, Principles of Polymerization, 1991), and the use of the term herein is consistent with the commonly understood usage. Statistical copolymers are derived from the simultaneous polymerization of two monomers and have a distribution of the two monomer units along the copolymer chain that follows Bernoullian (zero-order Markov), or first or second order Markov statistics. The polymerization may be initiated by free radical, anionic, cationic or coordinatively unsaturated (e.g., Ziegler-Natta catalysts) species. According to Ring et al., (Pure Appl. Chem., 57, 1427, 1985), statistical copolymers are the result of elementary processes leading to the formation of a statistical sequence of monomeric units (that) do not necessarily proceed with equal probability. These processes can lead to various types of sequence distributions comprising those in which the arrangement of monomeric units tends toward alternation, tends toward clustering of like units, or exhibits no ordering tendency at all. Bernoullian statistics is essentially the statistics of coin tossing; copolymers formed via Bernoullian processes have the two monomers distributed randomly and are referred to as random polymers. For example, it is possible in a free radical copolymerization for the active end, in the case of one embodiment, a styryl or butadienyl radical, to have essentially no selectivity for styrene vs. butadiene. If so, the statistics will be Bernoullian, and the copolymer obtained will be random. More often than not, there will be a tendency for the propagating chain end to have some selectivity for one monomer or the other. In rare cases block copolymers can be derived from the simultaneous copolymerization of two monomers when the preference of the propagating chain ends for adding the opposite monomers is very low. The resulting polymer would be categorized as a block copolymer for the purposes of the present invention.



[0014] Statistical copolymers generally display a single glass transition temperature. Block and graft copolymers typically display multiple glass transitions, due to the presence of multiple phases. Statistical copolymers are, therefore, distinguishable from block and graft copolymers on this basis. The single glass transition temperature reflects homogeneity at the molecular level. An additional consequence of this homogeneity is that statistical copolymers, such as those of styrene and butadiene, when viewed by electron microscopy, display a single phase morphology with no microphase separation. In contrast, block and graft copolymers of styrene/butadiene, for example, are characterized by two glass transition temperatures and separation into styrene-rich domains and butadiene-rich domains. It should be noted that membranes of the invention which are produced from statistical copolymers originally having a single glass transition temperature and a single phase morphology do not necessarily exhibit a single phase morphology or a single glass transition temperature after sulfonation because of chemical changes in the polymer effected by the sulfonation, in combination with the physical changes effected by the casting processes of the invention.

[0015] The humidity-conducting polymers for use in the humidity exchange cells of the present invention are derived from the polymerization of arylvinyl monomers and which, therefore, contain pendant aryl or aromatic moieties. Arylvinyl monomers are defined herein as monomers that contain a vinyl group substituted with an aryl, haloaryl or alkyl-substituted aryl group. An example of a monomer containing a vinyl group substituted with an aryl is styrene, an example of a monomer containing a vinyl group substituted with a haloaryl group is chlorostyrene, and examples of monomers containing a vinyl group substituted with an alkyl-substituted aryl group are p-octylstyrene and vinyl toluene. One or more arylvinyl monomers may be copolymerized with olefin comonomers to produce a polymer which may be sulfonated; the resulting sulfonated copolymers may be used to form the membranes of the present invention.

[0016] Suitable arylvinyl monomers that can be employed to prepare the polymers for sulfonation include, for example, styrene, vinyl toluene,  $\alpha$ -methylstyrene, t-butyl styrene, chlorostyrene and all isomers of these compounds. Particularly suitable such monomers include styrene and lower alkyl- or halogen-substituted derivatives thereof. Preferred monomers include styrene,  $\alpha$ -methyl styrene, the lower alkyl- ( $C_1$ - $C_4$ ) or phenyl-ring substituted derivatives of styrene, such as for example, ortho-, meta-, and para-methylstyrene, the ring halogenated styrenes, para-vinyl toluene or mixtures thereof, and the like. A more preferred arylvinyl monomer is styrene. Residues derived from vinyl toluene and chlorostyrene may be less readily sulfonated than those from styrene; therefore, it may be desirable to include utilize vinyl toluene and chlorostyrene along with arylvinyl monomers that result in residues that may be more readily sulfonated, such as styrene or  $\alpha$ -methyl styrene, rather than as the sole arylvinyl component of the polymer. The aryl or aromatic moieties may be sulfonated at one or more positions on the aromatic rings to yield polymer chains having pendant aryl sulfonate groups.

[0017] Humidity-conducting polymers may also include residues derived from at least one olefin monomer, in addition to those derived from at least one arylvinyl monomer. Preferred olefin monomers include monoolefins, such

as  $\alpha$ -olefins and strained ring olefins, and diolefin monomers such as butadiene and isoprene.  $\alpha$ -Olefins include ethylene and  $C_{3-10}$  olefins having ethylenic unsaturation in the  $\alpha$ - or 1-position, such as ethylene, propylene, butylene, and isobutylene. Suitable  $\alpha$ -olefins include for example,  $\alpha$ -olefins containing from 3 to about 20, preferably from 3 to about 12, more preferably from 3 to about 8 carbon atoms. Particularly suitable are ethylene, propylene, butene-1,4-methyl-1-pentene, 1-hexene or 1-octene or ethylene in combination with one or more of propylene, 1-butene, 4-methyl-1-pentene, 1-hexene or 1-octene. These  $\alpha$ -olefins do not contain an aromatic moiety. Preferred monoolefin monomers are ethylene, propylene, 1-butene, 2-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, and 1-octene. Preferred strained ring olefins are the various isomeric vinyl-ring substituted derivatives of cyclohexene and substituted cyclohexenes, norbornene and  $C_{1-10}$  alkyl or  $C_{6-10}$  aryl substituted norbornenes, including 5-ethylidene-2-norbornene. Especially suitable are 1-, 3-, and 4-vinylcyclohexene, norbornene and 5-ethylidene-2-norbornene. Simple linear non-branched  $\alpha$ -olefins including, for example,  $\alpha$ -olefins containing from 3 to about 20 carbon atoms such as propylene, butene-1,4-methyl-1-pentene, hexene-1 or octene-1 are not examples of strained ring olefins. Preferred statistical arylvinyl polymers are ethylene/styrene, ethylene/propylene/styrene, ethylene/styrene/norbornene, and ethylene/propylene/styrene/norbornene copolymers.

[0018] The polymer may also contain residues derived from other comonomers, for example, acrylate monomers. In addition, copolymers derived from diolefins, for example, butadiene and isoprene copolymers may contain residual unsaturation. These are typically hydrogenated, or reduced, prior to being sulfonated. The sulfonated copolymers may be blended with other sulfonated copolymers or with conventional polymers in order to form composite membranes for use in the present invention.

[0019] A humidity-conducting polymer for use in a humidity exchange cell of the present invention typically contains at least 20 weight % of residues derived from styrene. More preferably, the copolymer contains from 20 to 50 weight % styrene, and most preferably, about 45 weight % styrene. The range of weight average molecular weight ( $M_w$ ) of the polymer of the invention is from about 20,000 grams/mole to about 1,000,000 grams/mole, and preferably from about 50,000 grams/mole to 900,000 grams/mole. The sulfonated polymer used for the membranes of the present invention are preferably water-insoluble. Water-insoluble is defined as having a solubility of less than 0.5 grams of polymer in 100 grams of water at 100° C. Suitable humidity-conducting polymers include sulfonated, block styrene-ethylene-butylene-styrene copolymers, sulfonated, reduced, statistical styrene-butadiene copolymers and sulfonated statistical styrene-ethylene copolymers. Statistical styrene-butadiene copolymers may be obtained from Goodyear; block styrene-ethylene-butylene-styrene copolymers may be obtained from Shell and statistical ethylene-styrene copolymers (ethylene styrene interpolymers (ESI)) may be obtained from Dow Chemical. The Dow ESI polymers include the pseudo-random interpolymers as described in EP-A-0,416,815 by James C. Stevens et al. and U.S. Pat. No. 5,703,187 by Francis J. Timmers, both of which are incorporated herein by reference in their entirety.



[0020] Where diolefins are used as comonomers, the unsaturated residues in the copolymer membranes of the invention are may selectively hydrogenated prior to sulfonation of aromatic groups derived from the styrene residues. The amount of unsaturation remaining after hydrogenation is less than 5 percent of the starting level of unsaturation, and preferably less than 3 percent of the original. Statistical copolymers of styrene and butadiene, also known as styrene-butadiene rubber, or SBR may be used. The copolymer may be hydrogenated by methods known in the art, such as hydrogen gas in the presence of catalysts such as Raney Nickel, and platinum or palladium metals. The diimide reduction described in the examples may also be employed to produce materials that are useful as ion-conducting membranes. Hydrogenated statistical copolymers of styrene and butadiene are also commercially available. Oxidation of residual unsaturated sites in the polymer at levels greater than 5 percent unsaturation leads to degradation of the polymer and shortens the useful life of the membrane under operating conditions.

[0021] The hydrogenation level may be determined by the method of Parker et al. An FTIR spectrum of a hydrogenated styrene butadiene copolymer is analyzed by measuring the heights of the peaks at  $963\text{ cm}^{-1}$  and  $1493\text{ cm}^{-1}$ , corresponding to the absorbance of  $=\text{CH}$  and  $-\text{CH}_2$ , respectively. The percent hydrogenation is calculated using the following equation:

$$\% \text{ hydrogenation} = -15.71x + 99.4$$

[0022] where  $x$ =the ratio of the peak height at  $963\text{ cm}^{-1}$  to the peak height at  $1493\text{ cm}^{-1}$

[0023] A sulfonation process for styrene copolymers is described in U.S. Pat. Nos. 5,468,574, 5,679,482, and 6,110,616. The preferred level of sulfonic acid functionality ranges from about one functional group per five aromatic rings (20 mol %) to about four functional groups per five aromatic rings (80 mol %), such that the equivalent weight of the resulting sulfonated polymer is from about 100 grams/sulfonate equivalent to about 1000 grams/sulfonate equivalent. For example, for a copolymer of 45 weight percent styrene, the preferred range is between one sulfonic acid group per five styrene units (20 mol %, equivalent weight=1200 grams/equivalent) to about four sulfonic acid group per five styrene units (80 mol %, equivalent weight=300 grams/equivalent). Equivalent weight may be further limited to 400-700, and even further limited to 520-690. For a copolymer of 30 weight percent styrene, the preferred range is between one sulfonic acid group per four styrene units (25 mol %, equivalent weight=1400 grams/equivalent) to four sulfonic acid groups per five styrene units (80 mol %, equivalent weight=430 grams/equivalent). The sulfonation level of the polymer may be controlled by the stoichiometric ratio of the sulfonating agent, acetyl sulfate, to the styrene content of the polymer. For example, addition of 1.0 equivalents of acetyl sulfate yields a polymer of 32 mol % sulfonation and 1.4 equivalents yields 44 mol % sulfonation.

[0024] The HUX membrane is a hydrocarbon hydrophilic polymer that possesses a low equivalent weight, from 1000 down to 100, preferably 700 down to 300 and most preferably 690 down to 380. Partially sulfonated styrene-olefin copolymers are generally preferred. Specifically, styrene-ethylene and styrene-hydrogenated butadiene, isoprene or equivalent olefinic copolymers that possess a random, alter-

nating, segmented or statistical in monomer distribution along the chain are preferred. Pseudo-random is a subclass of statistical; a weighted change in the monomer incorporation that skews the distribution from a random arrangement (i.e. Bernoullian) is defined as statistical. Linear arrangements have been described here, but branched or grafted including star arrangements of monomers are possible as well. In addition, block copolymers of styrene and hydrogenated butadiene, isoprene, or equivalent olefin can be employed. The block architecture can be diblock, triblock, graft-block, multi-arm starblock, multiblock, segmented or tapered block.

[0025] The HUX support material is preferably, but not limited to, a polyolefin, spaced-member, fiber netting. Fiber extrusion followed by melt bonding is a common method to prepare the netting, however, other methods can be used by themselves or in combination. These include injection molding, compression molding, fiber extrusion with solvent bonding, spin bonding, and ultrasonic welding.

[0026] Suitable materials for the reinforcing substrate include woven, nonwoven, knit and cross-laid fabrics; in the context of the present invention, the term 'fabrics' is defined as including meshes and nettings. Microporous films may also be used. The fabric of a reinforcing substrate may be composed of synthetic fibers or filaments, glass yarns, non-corroding metal fibers, such as nickel fibers, or carbon fibers. The fibers, filaments or yarns should be ones to which the water-conducting polymer film adheres strongly. Suitable synthetic fibers include polyolefins, particularly polyethylene or polypropylene, and polyesters. The fibers may have organic or inorganic sizing agents or coupling agents applied, including polyvinylalcohol, starches, oil, polyvinylmethylether, acrylic, polyester, vinylsilane, aminosilane, titanate, and zirconate. Silicone-based lubricants are sometimes employed for greater tear strength. A microporous film may be composed of any synthetic polymer to which the humidity-conducting polymer adheres. In particular, the films may have a polyolefin composition, and more particularly, polyethylene. Films having a fluoropolymer composition may also be used. A composite membrane for use in a humidity exchange cell according to the present invention may be prepared by impregnating the substrate with a humidity-conducting polymer. This may be done by any of several known methods. These methods include direct coating, wherein a solution of the humidity-conducting polymer in a suitable solvent, such as a lower alcohol, in particular, methanol or propanol. The benefit of direct coating is that it reduces the number of sub-assemblies and parts and, thus, reduces costs. Low cost fabrication is an object of the invention. Indirect coating methods, such as solution casting, may also be used.

[0027] Sequential buildup facilitates the manufacturing of the overall composite; coating is typically continued until a homogenous sheet is formed when reinforcement may or may not be completely coated. Formulations that readily wet the substrate are available at low cost and produce composites without holes or other defects are preferred. Alternatively, the water-conducting polymer may be applied to the reinforcing substrate by hot roll laminating it with reinforcing substrate, thus eliminating the need for multiple coating passes. The water-conducting polymer film may also contain a ceramic filler, if desired. Finally, a composite membrane composed of nonwoven fabric may be manufactured by



adding staple-pulped fiber to solution of the water conducting polymer, and coating on a release substrate.

**[0028]** The humidity-conducting polymer may contain one or more additives, including crosslinking agents, flame retardants (suppressants and synergists), biocides (mildewicides, fungicides, anti-mold agents, antiviral agents, bacteriocides, anti-parasitic agents, and insecticides.), plasticizers, uv stabilizers (uv absorbers, and light stabilizers), antioxidants (primary or secondary) and thermal stabilizers. Any one compound may impart one or more characteristic enhancements. The basic requirements are that (a) the additive is miscible with the hydrophilic polymer, (b) it does not compromise the mechanical strength or integrity of the membrane in the cell, (c) it not reduce the performance (e.g. moisture transfer effectiveness) or lifetime of the cell in the application. Therefore, these are objects (a, b, c) of the invention. Although not an object, it is desirable that the additive, retain the activity and efficacy of said characteristic when present with the polymer in the formulation.

**[0029]** For biocides, our principal concern is mold and mildew growth because of the potentially low, local pH of these sulfonated hydrophilic polymers. However, resistance to other possible biological agents such as fungus, bacteria, viruses, parasites, insects or protozoa is desirable. Any biologicals that reduce the available surface area of the membrane for transfer of moisture from the stream must be prevented. Compatible chemical agents are 10,10'-oxybisphenoxarsine available from Rohm and Haas in a liquid or resin carrier under the tradename Vinyzene. An arsenic-free alternative is 4-chloro-3,5-dimethyl phenol an organic chemical available from Aldrich. These can be used effectively at loadings up to 5.0 phr. However, Dow Chemical's fungicide AMICAL 48 and bactericide BIOPAN BP PLUS, both toxic metal-free are preferred.

**[0030]** Flame retardancy is important insofar as additives can reduce the tendency of the cell to catch fire, spread a fire and to reduce smoke emissions. For pure liquid streams the threat of fire does not present itself, except for air/water or some other highly polar gas vapor streams at low humidity. For these applications, a non-halogen flame retardant (basically a flame inhibitor) is typically used for polyolefins. This is available from Unitex chemical under the tradename Uniplex FRX 44-94S. Bromine-containing retardants, Uniplex BAP-755 (brominated alkyl phosphate) and Uniplex FRP-64 (poly (2,6-dibromophenylene oxide)) are also viable. For high performance, the polymeric, flame retardant is desirable but it requires a synergist, for which the high phosphorous-containing FRX 44-94S is suitable. However, Great Lakes Chemicals' tetrabromobisphenol A is preferred for polymer solubility.

**[0031]** Organophosphates serve as hydrophilic plasticizers that function by increasing the water or some other highly polar liquid retention of the membrane in HUX cell in the application environment. The increased water or some other highly polar liquid content may improve performance by increasing membrane permeability as well as reduce flammability, since substantially more water or some other highly polar liquid must evaporate before flames may spread to the cell. In the process, the evaporation of water or some other highly polar liquid suppresses smoke. Also, these can potentially function as synergists for bromine-containing flame retardants. These are trialkyl phosphates, such as

trimethyl phosphate, triethyl phosphate, tripropyl phosphate and tris(2-ethyl hexyl) phosphate.

**[0032]** Antioxidants (and thermal stabilizers) can increase shelf life of HUX cells by circumventing the auto-oxidation of the hydrophilic polymer during storage. However, a more important advantage is the ability to reduce oxidation of the sulfonated hydrophilic polymer in the HUX cell during operation since at low humidity the polymer is continuously subject to the transfer of heat and thus, will see temperatures as high as 37° C. Oxidation of organic impurities may result and reduce performance this be minimized with the use of antioxidants. These are basically hindered phenols of high molecular weight and include: stearyl-3-(3',5'-di-tert-butyl-4-hydroxyphenyl) propionate (BNX 1076) and tetrakis[methylene-3 (3',5'-di-tert-butyl-4-hydroxyphenyl)propionate] methane (BNX 1010) both available from Mayo Corp. and poly(phenol-formaldehyde) novalac resin (HRJ-12700) available from Schenectady International. Peroxide decomposers add benefit as synergists to hindered phenols, these are aryl phosphites; such as Tris(2,4-ditert-butylphenyl) phosphite (Benafos 1680). UV stabilizers are important for outdoor applications; these are light absorbers with a broad absorption range of which benzotriazoles are preferred. Ciba's Tinuvin 384-2 (Benzene propionic acid (3-2H-benzotriazol-2-yl)-5-(1,1-di-methylethyl-4)-hydroxy, C7-C9-branched and linear alkyl esters) is suitable because of good thermal and environmental stability. Hindered amine light stabilizers (HALS) may be suitable. However, free amines form salts that may reduce water or some other highly polar liquid transport, these are less preferred. Therefore, nitroso-alkyl and specifically nitroso-alkyl ethers containing HALS are preferred for these polymers to maximize their effectiveness as stabilizers.

**[0033]** Further improvements in mechanical strength and integrity especially at saturation (dehydration or hydration), or when one (separation, dehydration, hydration) or both sides (osmosis, filtration or dialysis) of the membrane are in contact with liquid water or some other highly polar liquid can be obtained through the formation of crosslinks between the polymer chains in the membrane. There are principally two types of crosslinking approaches: (a) crosslinks through carbon-containing groups and (b) crosslinks through sulfur-containing groups.

**[0034]** The first approach (or Type I) is small molecule coupling of two chains through polymeric chain radicals. The polymeric chain radicals are created by reaction of olefinic (or styrenic) units with primary radicals (formed from the thermal decomposition of peroxides, or created by scission and/or ionization of the olefinic units by UV, e-beam, gamma-ray, high energy particles. The polymeric chain radicals form bonds to maleimide by addition to double bonds or by radical coupling. Reaction of two such chains with the single molecule forms a crosslink. N,N'-1,3-Phenylene-dimaleimide is a preferred example. Peroxide initiators are benzoyl peroxide, 1,1-Di-(tert-butylperoxy)-3,3,5-trimethylcyclohexane, and 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3.

**[0035]** The high levels of initiator (if below the solubility limit in the polymer) required for the achievement of a dense interconnected network of chains likely leads to primary radical termination of low mobility polymeric chain radicals. Also, cross-linking agents that form stable chain radi-



cals consume initiator without formation of the polymeric chain radicals necessary for the dense network. Co-agent radicals must be of similar reactivity to polymer chain radicals for coupling of adjacent polymer chains. More important, however, is that a substantial concentration of polymeric chain radicals are formed. Initiators are chosen that decompose to highly reactive radicals at moderate temperatures with a very high rate of initiation. The degree of crosslinking necessary to form a 'tight' interconnected network of chains depends on a large variety of factors. The initiator type: functionality, primary radical reactivity, initiation efficiency, coupling or crosslinking agent type; crosslinking mechanism, specific interaction with polymer, microstructure of the polymer; reactivity of polymer radical, mobility and concentration of radicals which is controlled for the most part by temperature and/or where applicable the light intensity for photoinitiation or photosensitization.

[0036] Organometallic crosslinking agents of the enolate-type also fare well when used in conjunction with the more reactive alkyl peroxides as initiators. The more stable benzoyl and isobutyl peroxide radicals tend to have low initiation efficiencies for crosslinking but if high concentrations of initiator can be achieved by increasing solubility in the polymer then these can be suitable. Organometallic agents of chelated metals that possess multiple stable oxidation states are promising, such as metal diketonates or derivatives thereof. Aluminum acetoacetate is a preferred example. Provided the metals are redox-active in the chelated state, these can potentially catalyze decomposition of peroxides or serve as photoactivators or sensitizers for photoinitiators. Useful peroxide initiators are benzoyl peroxide, 1,1-Di-(tert-butylperoxy)-3,3,5-trimethylcyclohexane, and 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3. These can crosslink in conjunction with other agents or alone with heat, ultraviolet, visible light, e-beam, high energy particle bombardment, such, alpha particles, ionizing radiation such as gamma rays and by electric discharge such as plasma.

[0037] The list includes but is not limited to: initiators; 1,1-Di-(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3, tert-butyl peroxide, dicumyl peroxide, methyl ethyl ketone peroxide, metachloroperoxybenzoic acid, benzoyl peroxide; crosslinking agents (includes coupling agents); aluminum acetylacetonate, cobalt(III) acetylacetonate, cobalt(II) acetylacetonate, nickel ketene acetals, N,N'-1,3-phenylene-dimaleimide, divinyl sulfone, trispropargyl benzene, divinyl benzene, vinyl triethoxy silane, hexamethyldisilazane, trimethylolpropane trivinyl ether, trimethylolpropane trimethacrylate, trimethylolpropane allyl ether, triallyl cyanurate, and triallyl phosphate.

[0038] The second approach (or Type II) is sulfonamide crosslinking. The reaction of sulfonyl-imidazole or equivalent with aromatic amines results in sulfonamide linkage between styrene units. The reaction of a styrene sulfonic acid unit of the polymer chain with 1,1'-carbonyl diimidazole forms styrene sulfonyl imidazole. The imidazole molecule is a good leaving group so even moderate nucleophiles such as, aromatic diamines displace them. A suitable aromatic diamine is 4-aminophenylsulfone.

[0039] The principal advantage of both types of crosslinking schemes is that the crosslinking agents may be added to a solution of the polymer, mixed in, and cast normally.

Subsequently the HUX cell may be dried in an oven to remove residual solvent, heated in an oven, or exposed to radiation. It is an object of the invention that the additives be simply incorporated into the formulation.

[0040] FIG. 2 is a partially exploded view of a humidity exchange cell or ventilator core 20 including a composite membrane 10, a first chamber 22 for containing a first fluid, a second chamber 24 for containing a second fluid and a number of spacers or ribs 16 which are adhered to membrane 10. Cell 20 includes a series of alternating first and second chambers. A cap 26 may be used to enclose the topmost and/or bottommost chambers.

[0041] The membranes 10 are stacked one on top of another to form ventilator core 20 as shown in FIG. 2. The orientation of the each layer is rotated by 90 degrees as it is put down into the core. This forms the cross-flow pattern for the exchange of heat and moisture within the core. Not shown, but fully realizable, is a counter-flow arrangement of the layers. Here the layers would be in a single orientation, with no rotation, in the core. A complex manifold would be designed to route gas streams to every other layer in the stack. These manifolds would be placed on opposite sides of the core. The non-manifold sides of the core could be sealed to the external environment if necessary.

[0042] Spacer 16, as shown in FIGS. 1 and 2, is configured as a series of ribs, typically adhered to the humidity-conducting polymer surface. These ribs may have a synthetic polymer composition, particularly, PVC, and may be rectangular or circular in cross-section. In other embodiments (not shown), spacer 16 may be a corrugated paper or plastic sheet. In some embodiments, spacer 16 may be a series of adhesive beads. The adhesive may be a hot-melt, cold-melt, or solid adhesive; it may be either thermoplastic or thermosetting. The HUX cell may possess certain specific sub-elements to be effective as a mass (i.e. moisture) exchanger. The basic sub-elements are as follows: (a) a hydrocarbon hydrophilic polymer membrane formulated to be highly permeable to water or some other highly polar liquid or gas, (b) a support matrix to impart mechanical integrity to the membrane and to maintain planarity during operation and (c) a manifold for the distribution of a fluid across the face of the membrane. The disclosed HUX cell is of unitary design in that it incorporates all three sub-elements into a complete cell structure that can be fabricated as a single unit. The device can be built up of this structure by simple stacking and securing the cells in an enclosure.

## EXAMPLES

[0043] A cross-flow sensible and latent heat exchanger was constructed. The membranes in the exchanger were made by laminating a nylon non-woven reinforcement to a layer of a sulfonated styrene-olefin polymer. The membranes were stacked on top of one another using a PVC spacer with an applied adhesive. The PVC spacers were oriented at 90 degrees to each other on alternating layers. Every other layer in the core had the same flow direction: 1, 3, 5, 7 etc. had the same flow direction while 2, 4, 6, 8, etc. had a flow direction that was oriented 90 degrees. The edges of each layer in the core were sealed with double-sided adhesive tape. The cross-flow exchanger was placed in a test apparatus where the flow rate, temperature, and moisture of two airflows could be controlled. One air flow had approxi-



mately a 90° F. temperature at a relative humidity of 55% of saturation. The other airflow was held at 70° F. and a relative humidity of 50% of saturation. The exchange of sensible and latent heat between the two airflows at different airflow rates was monitored. The data in graph form is shown in **FIG. 3**. The airflow is expressed is normalized as a function of the square feet of membrane area. This allows us to compare exchangers of various materials and exchangers against each other using the exchange area within the exchanger. The graph shows that over 70% total effectiveness for this type of exchanger can be achieved using sulfonated styrene-olefin polymer membranes.

What is claimed is:

1. A cell for transferring heat and moisture between a first fluid and a second fluid, said cell comprising:

at least one composite membrane, disposed between at least one first chamber for flow of the first fluid therethrough and at least one second chamber for flow of the second fluid therethrough;

whereby heat and moisture is transferable between the first fluid and second fluid via the composite membrane.

2. A cell according to claim 1, wherein said composite membrane comprises:

an at least partially sulfonated humidity-conducting polymer comprising residues derived from at least one arylvinyl monomer; and

a reinforcing substrate bonded thereto.

3. A cell according to claim 2, additionally comprising at least one spacer disposed on a surface of the composite membrane

4. A cell according to claim 3, wherein said at least one spacer comprises a dimension normal to the surface of the composite membrane corresponding to a height of the first chamber.

5. A cell according to claim 3, wherein a longitudinal axis of the at least one spacer is oriented parallel to a direction of flow of the first fluid in the first chamber.

6. A cell according to claim 5, wherein the direction of flow of the first fluid in the first chamber is orthogonal to a direction of flow of the second fluid in the second chamber.

7. A cell according to claim 5, wherein the direction of flow of the first fluid in the first chamber is opposite to a direction of flow of the second fluid in the second chamber.

8. A cell according to claim 3, wherein the at least one spacer comprises a plurality of synthetic polymer ribs.

9. A cell according to claim 3, wherein the at least one spacer comprises an adhesive composition.

10. A cell according to claim 3, wherein the at least one spacer comprises a corrugated sheet.

11. A cell according to claim 2, wherein said at least one composite membrane comprises a plurality of composite membranes, and said at least one first chamber and said at least one second chamber comprises a plurality of alternating first chambers and second chambers, each separated by a composite membrane.

12. A cell according to claim 2, wherein said reinforcing substrate comprises a nonwoven fabric.

13. A cell according to claim 2, wherein said reinforcing substrate comprises a microporous film.

14. A cell according to claim 2, wherein said reinforcing substrate comprises at least one synthetic fiber.

15. A cell according to claim 14, wherein said at least one synthetic fiber comprises at least one polyolefin.

16. A cell according to claim 2, wherein the humidity-conducting polymer additionally comprises an additive selected from the group of antioxidants, biocides, flame retardants, uv stabilizers, hydrophilic plasticizers, and mixtures thereof.

17. A cell according to claim 2, wherein the humidity-conducting polymer comprises at least one antioxidant, at least one biocide, and at least one flame retardant.

18. A cell according to claim 2, wherein the humidity-conducting polymer is crosslinked using a peroxide initiator and an organometallic enolate coupling agent.

19. A cell according to claim 18, wherein the peroxide initiator is 1,1-di-(tert-butylperoxy)-3,3,5-trimethylcyclohexane and the organometallic enolate coupling agent is aluminum acetoacetate.

20. A cell according to claim 18, wherein the peroxide initiator is 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3.

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