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(54) **DIRECT ASSEMBLY PROCESS FOR FABRICATION OF IONOMERIC POLYMER DEVICES**

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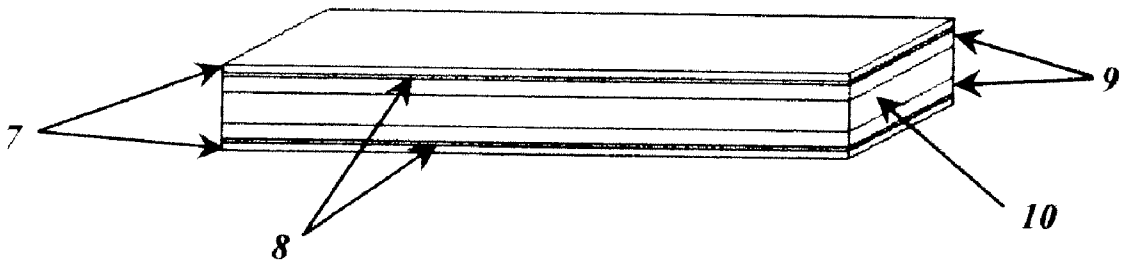
(57) **ABSTRACT**

Ionomeric polymer sensors, actuators, and transducers and methods for fabricating them are disclosed. One embodiment of the sensors, actuators, and transducers possess a high surface area electrode layer that is applied by hot pressing and a highly conductive surface layer. Another embodiment of these sensors, actuators, and transducers possess a high surface area electrode layer that is penetrated by electronically conductive nanowires. Methods for fabricating these sensors, actuators, and transducers are disclosed. These methods involve the formation of the high surface area layer from a liquid mixture that contains ionomeric polymer, electronically conductive particles, and possibly diluent. This mixture is formed into layers either directly on an ionomeric polymer, on a separate transfer decal, or on an electronically conductive layer. This electronically conductive layer may also include an array of nanowires. These electrode layers are then attached to an ionomeric polymer membrane by hot pressing. The ionomeric polymer membrane may be swollen with a diluent either prior to the hot pressing or after the hot pressing step. Also, the ionomeric polymer membrane may be formed by casting from a liquid mixture containing ionomeric polymer and diluent.



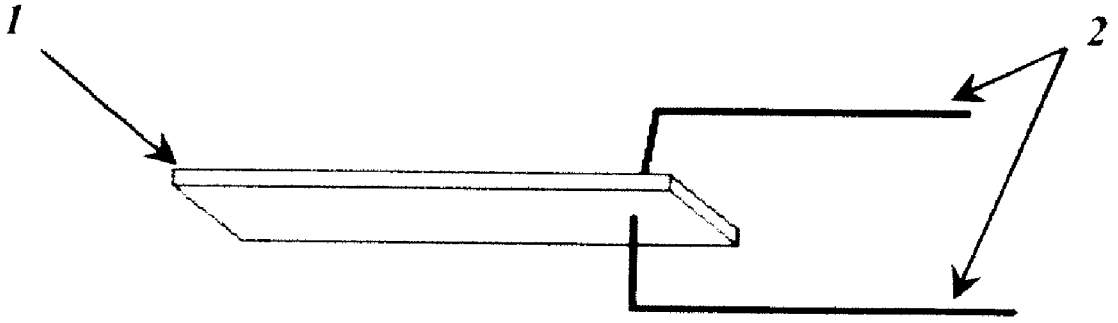


Figure 1

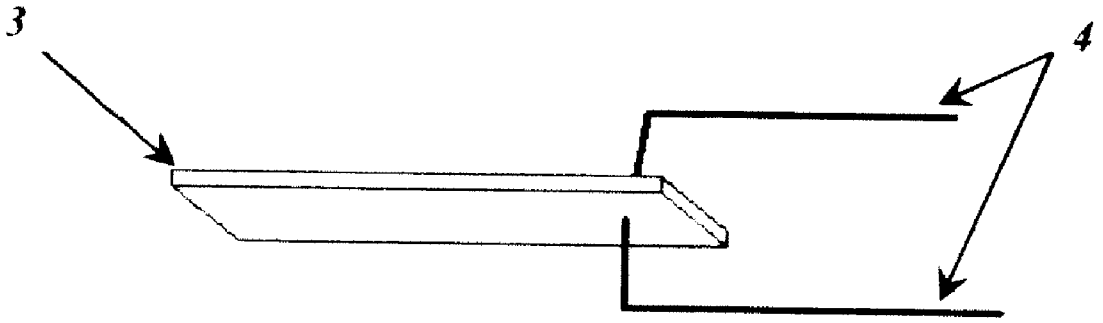
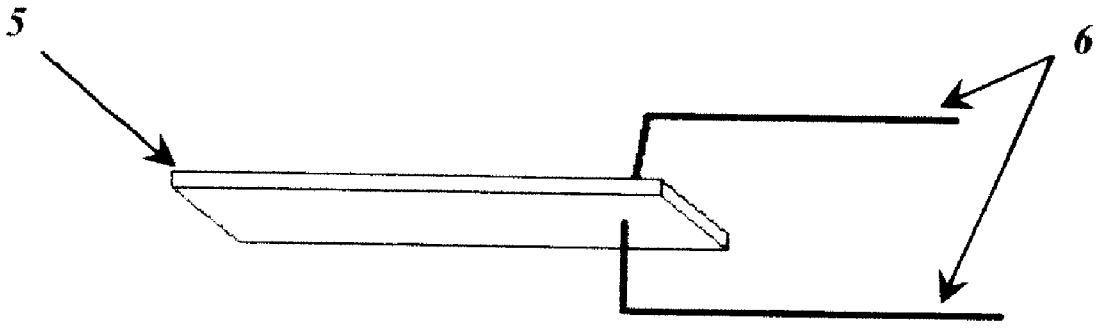


Figure 2



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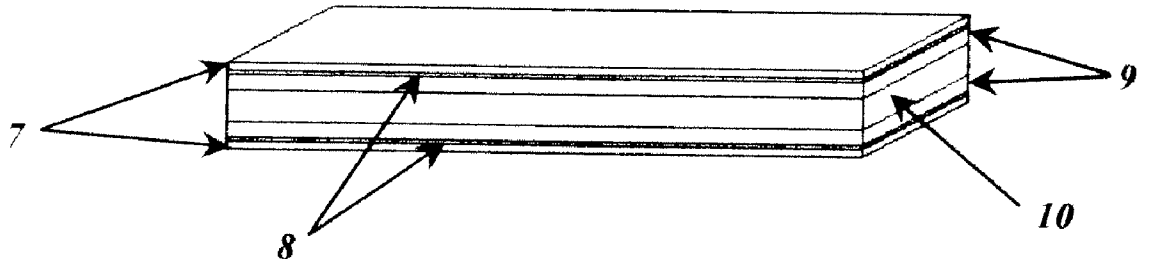

Figure 4

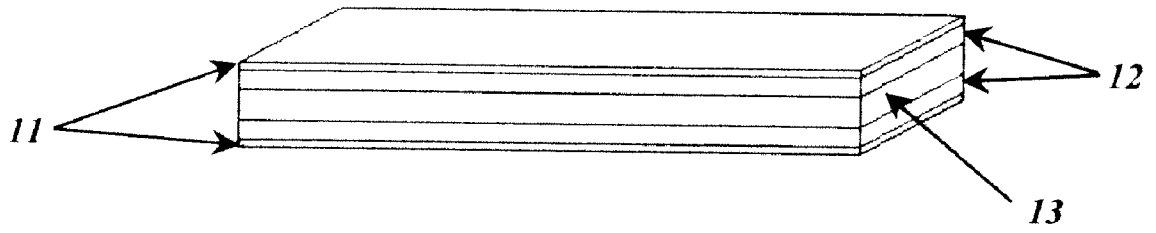

Figure 5

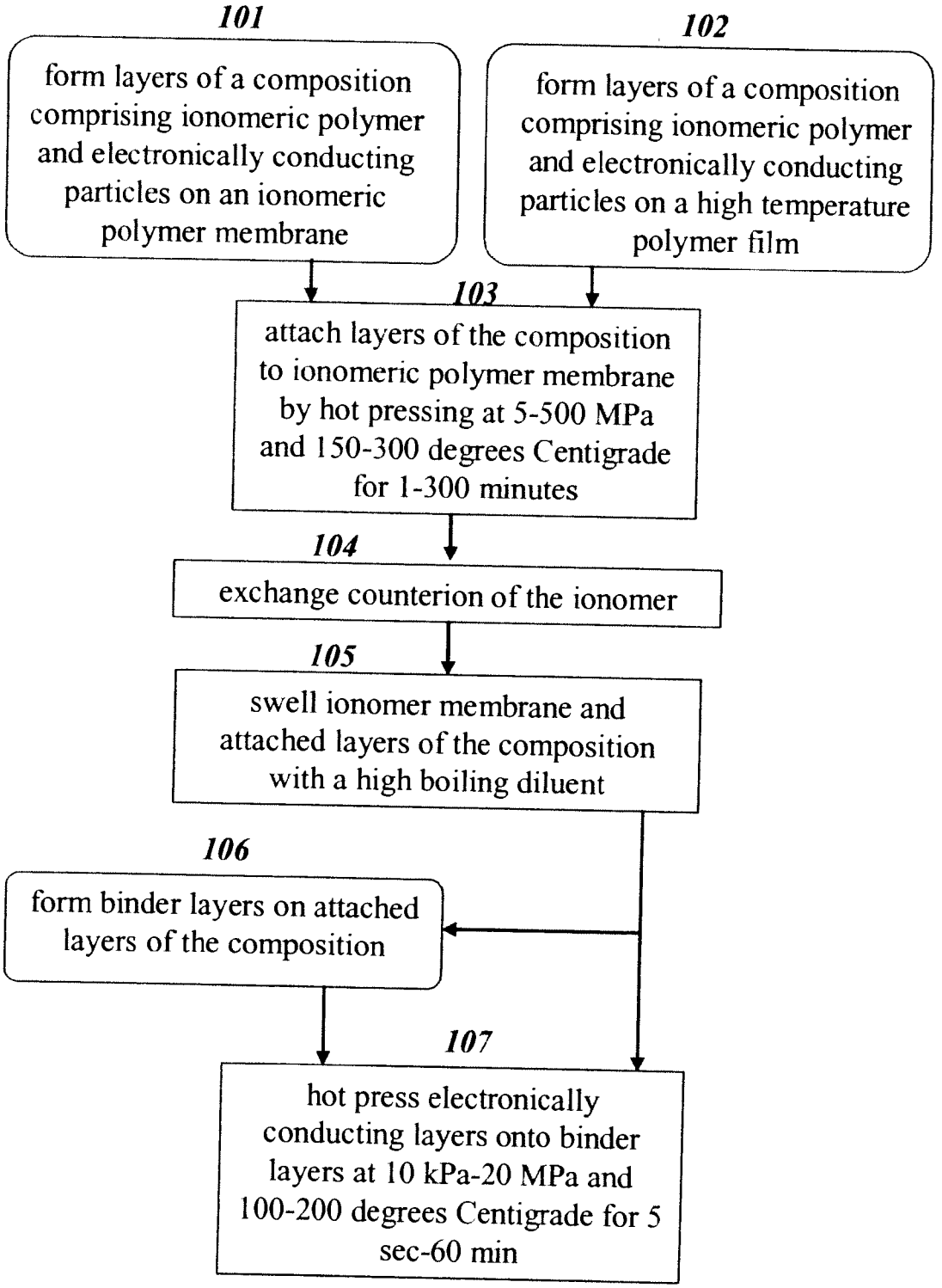
101
form layers of a composition comprising ionomeric polymer and electronically conducting particles on an ionomeric polymer membrane
102
form layers of a composition comprising ionomeric polymer and electronically conducting particles on a high temperature polymer film
103
attach layers of the composition to ionomeric polymer membrane by hot pressing at 5-500 MPa and 150-300 degrees Centigrade for 1-300 minutes
104
exchange counterion of the ionomer
105
swell ionomer membrane and attached layers of the composition with a high boiling diluent
106
form binder layers on attached layers of the composition
107
hot press electronically conducting layers onto binder layers at 10 kPa-20 MPa and 100-200 degrees Centigrade for 5 sec-60 min

Figure 6

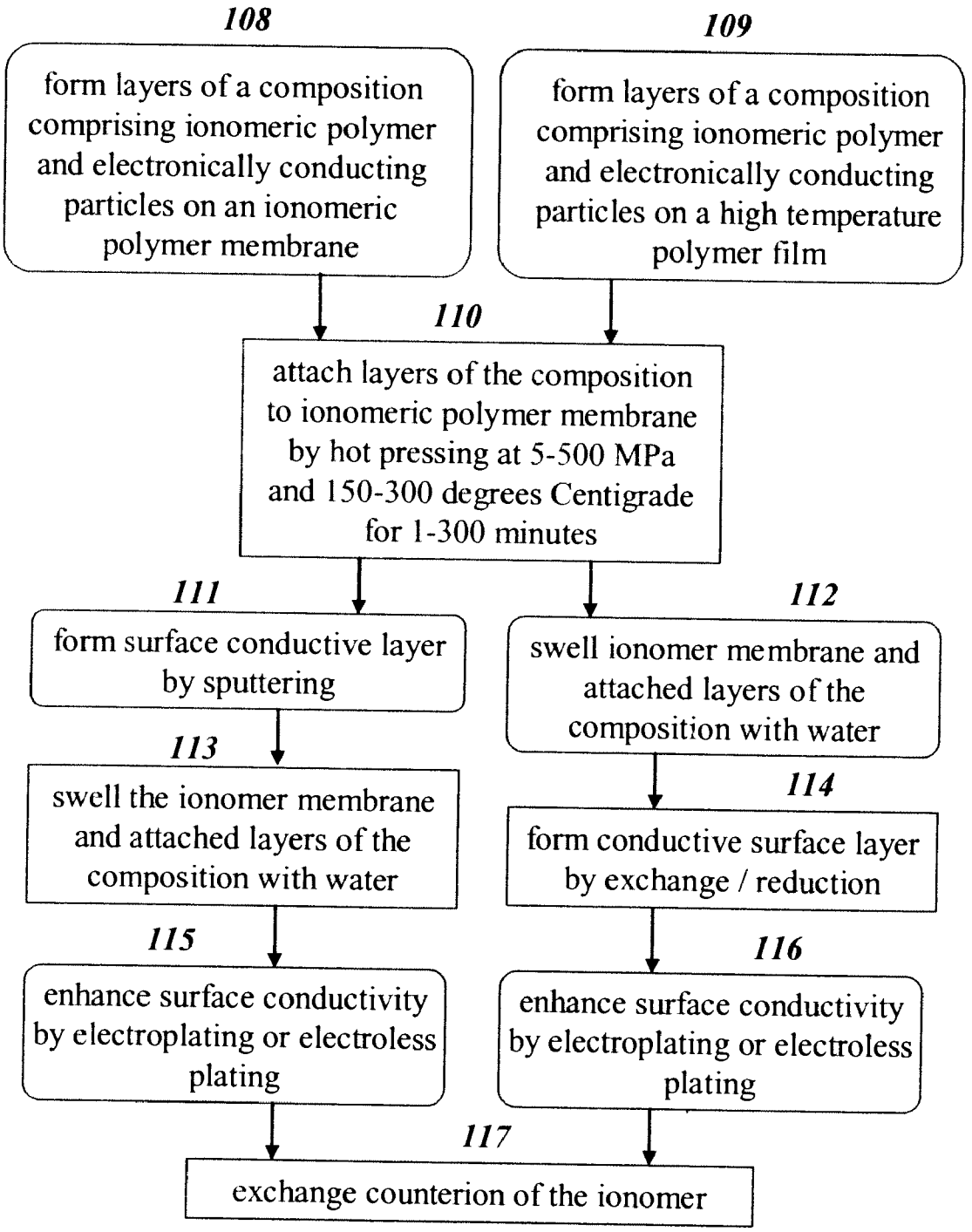
108
form layers of a composition comprising ionomeric polymer and electronically conducting particles on an ionomeric polymer membrane
109
form layers of a composition comprising ionomeric polymer and electronically conducting particles on a high temperature polymer film
110
attach layers of the composition to ionomeric polymer membrane by hot pressing at 5-500 MPa and 150-300 degrees Centigrade for 1-300 minutes
111
form surface conductive layer by sputtering
112
swell ionomer membrane and attached layers of the composition with water
113
swell the ionomer membrane and attached layers of the composition with water
114
form conductive surface layer by exchange / reduction
115
enhance surface conductivity by electroplating or electroless plating
116
enhance surface conductivity by electroplating or electroless plating
117
exchange counterion of the ionomer

Figure 7

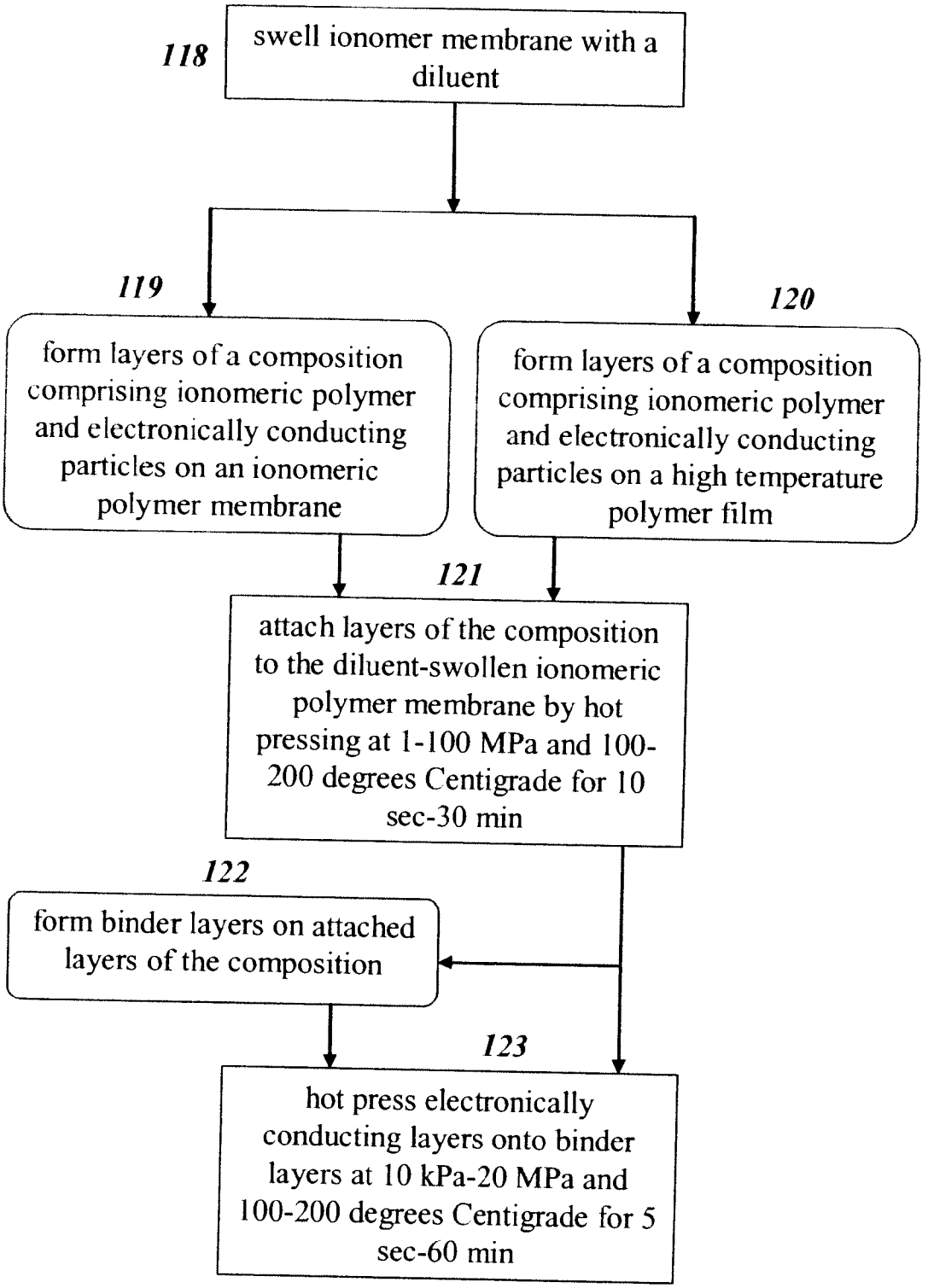
118
swell ionomer membrane with a diluent
119
form layers of a composition comprising ionomeric polymer and electronically conducting particles on an ionomeric polymer membrane
120
form layers of a composition comprising ionomeric polymer and electronically conducting particles on a high temperature polymer film
121
attach layers of the composition to the diluent-swollen ionomeric polymer membrane by hot pressing at 1-100 MPa and 100-200 degrees Centigrade for 10 sec-30 min
122
form binder layers on attached layers of the composition
123
hot press electronically conducting layers onto binder layers at 10 kPa-20 MPa and 100-200 degrees Centigrade for 5 sec-60 min

Figure 8

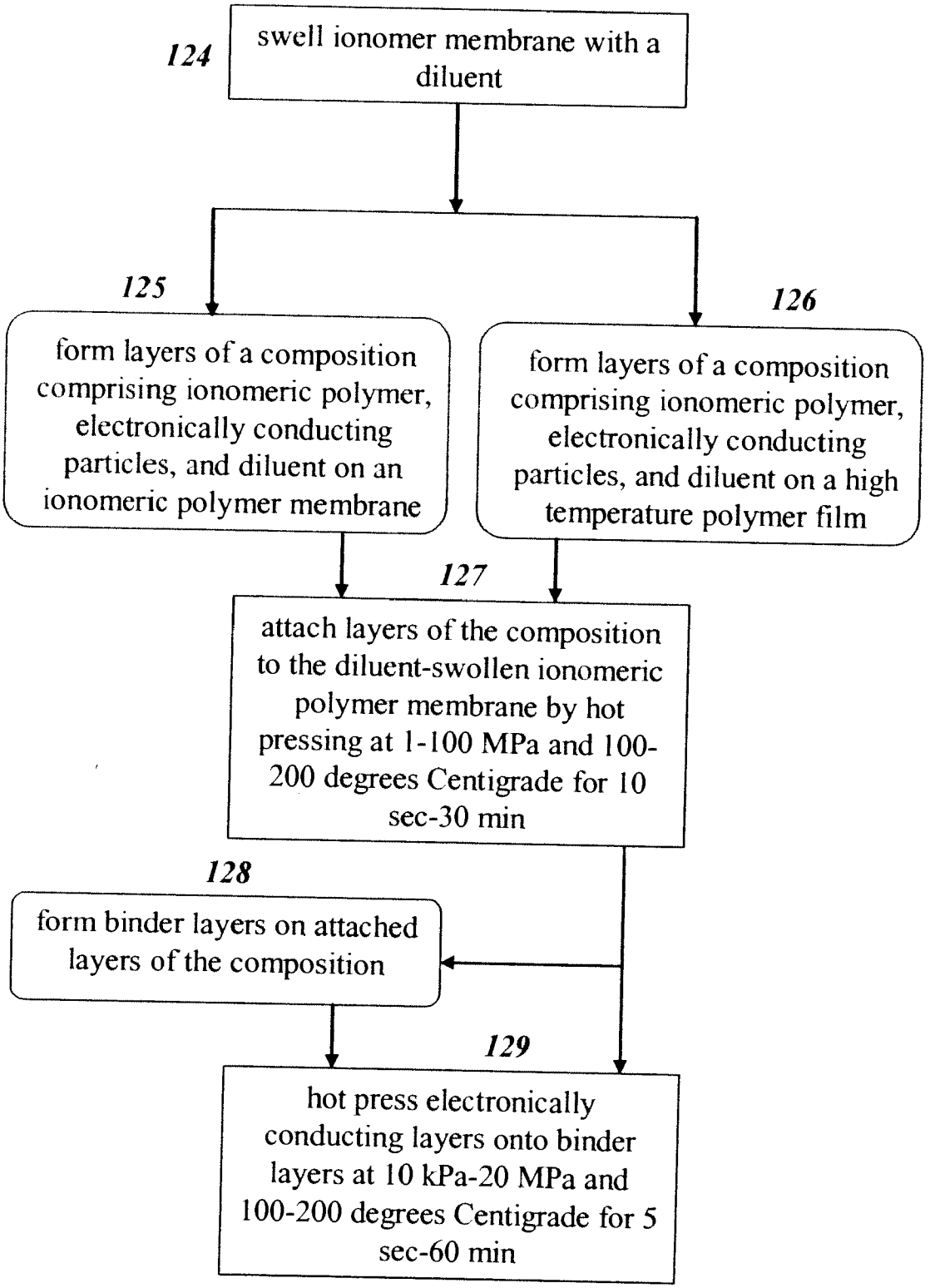
124
swell ionomer membrane with a diluent
125
form layers of a composition comprising ionomeric polymer, electronically conducting particles, and diluent on an ionomeric polymer membrane
126
form layers of a composition comprising ionomeric polymer, electronically conducting particles, and diluent on a high temperature polymer film
127
attach layers of the composition to the diluent-swollen ionomeric polymer membrane by hot pressing at 1-100 MPa and 100-200 degrees Centigrade for 10 sec-30 min
128
form binder layers on attached layers of the composition
129
hot press electronically conducting layers onto binder layers at 10 kPa-20 MPa and 100-200 degrees Centigrade for 5 sec-60 min

Figure 9

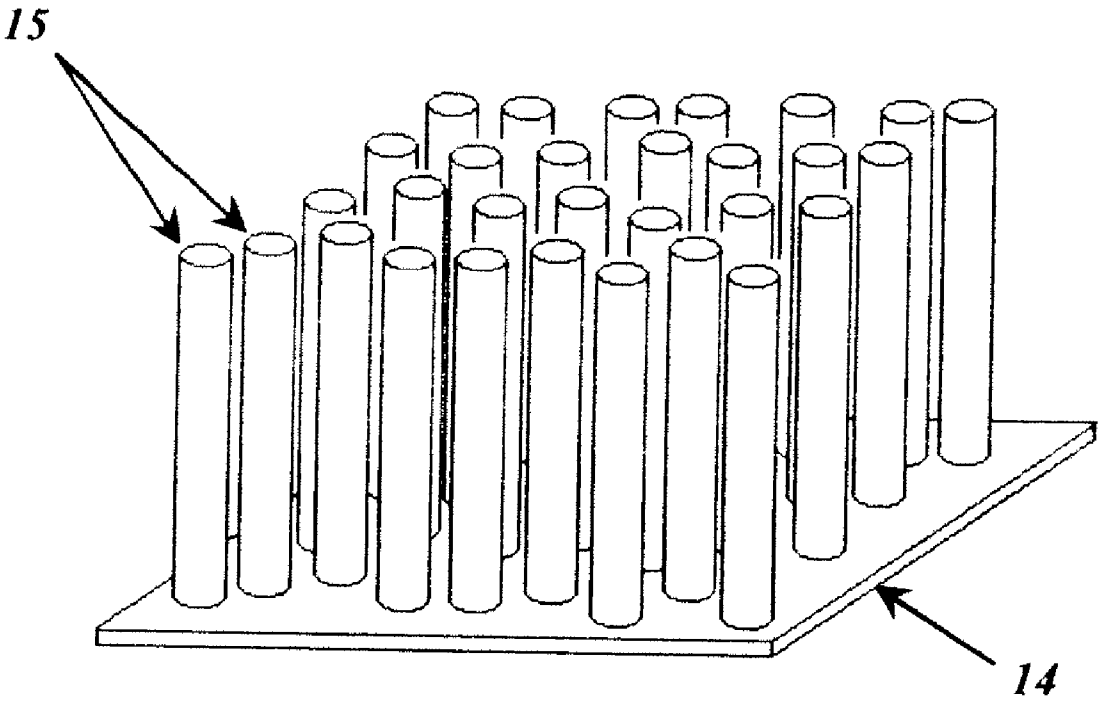

Figure 10

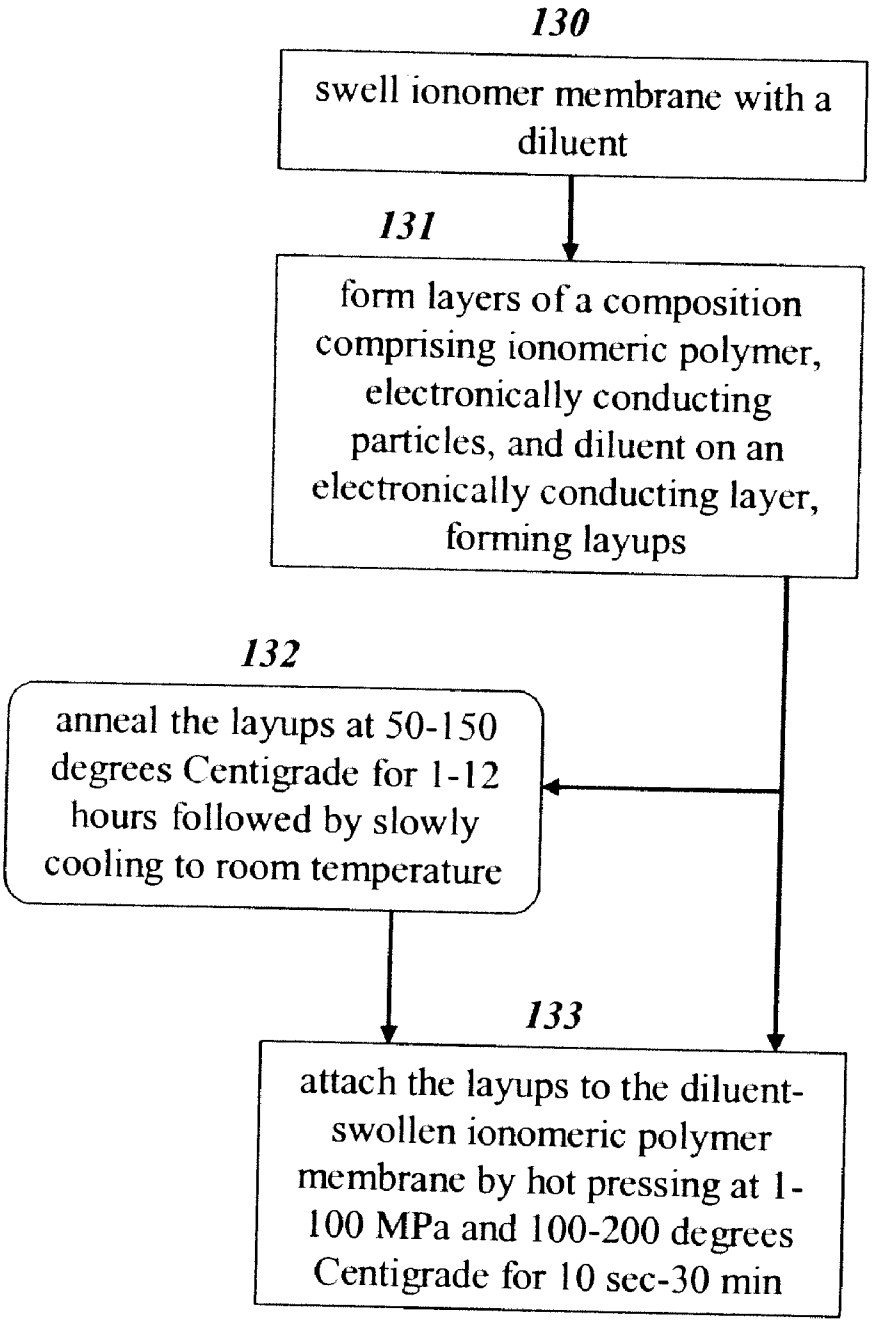
130
swell ionomer membrane with a diluent
131
form layers of a composition comprising ionomeric polymer, electronically conducting particles, and diluent on an electronically conducting layer, forming layups
132
anneal the layups at 50-150 degrees Centigrade for 1-12 hours followed by slowly cooling to room temperature
133
attach the layups to the diluent-swollen ionomeric polymer membrane by hot pressing at 1-100 MPa and 100-200 degrees Centigrade for 10 sec-30 min

Figure 11

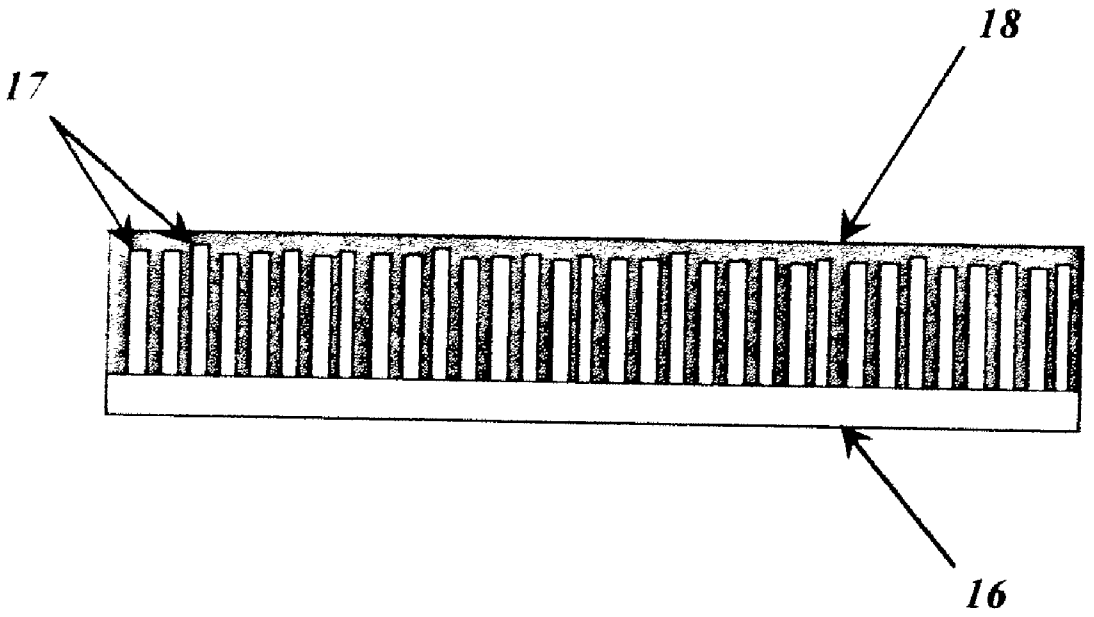

Figure 12

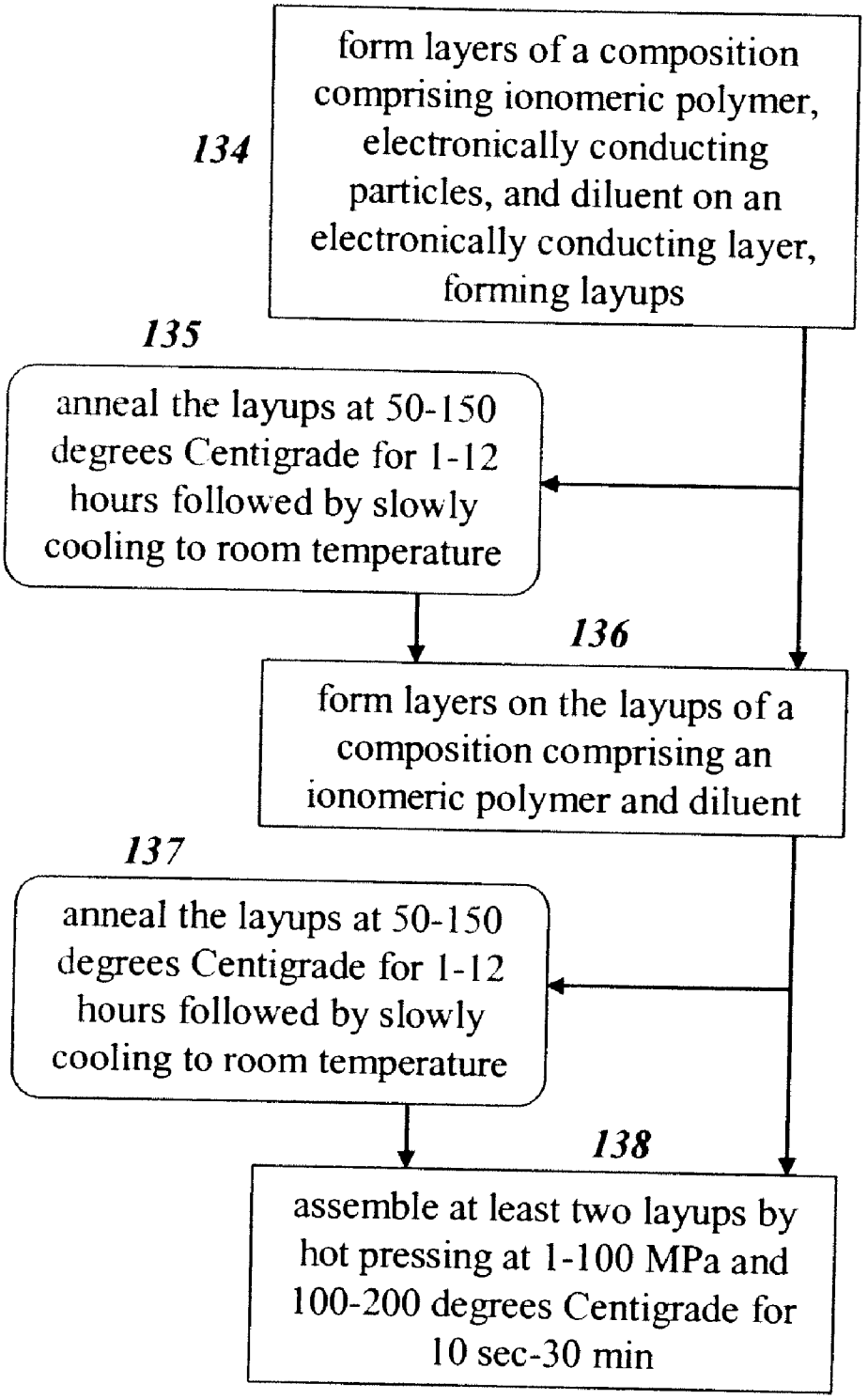
134
form layers of a composition comprising ionomeric polymer, electronically conducting particles, and diluent on an electronically conducting layer, forming layups
135
anneal the layups at 50-150 degrees Centigrade for 1-12 hours followed by slowly cooling to room temperature
136
form layers on the layups of a composition comprising an ionomeric polymer and diluent
137
anneal the layups at 50-150 degrees Centigrade for 1-12 hours followed by slowly cooling to room temperature
138
assemble at least two layups by hot pressing at 1-100 MPa and 100-200 degrees Centigrade for 10 sec-30 min

Figure 13

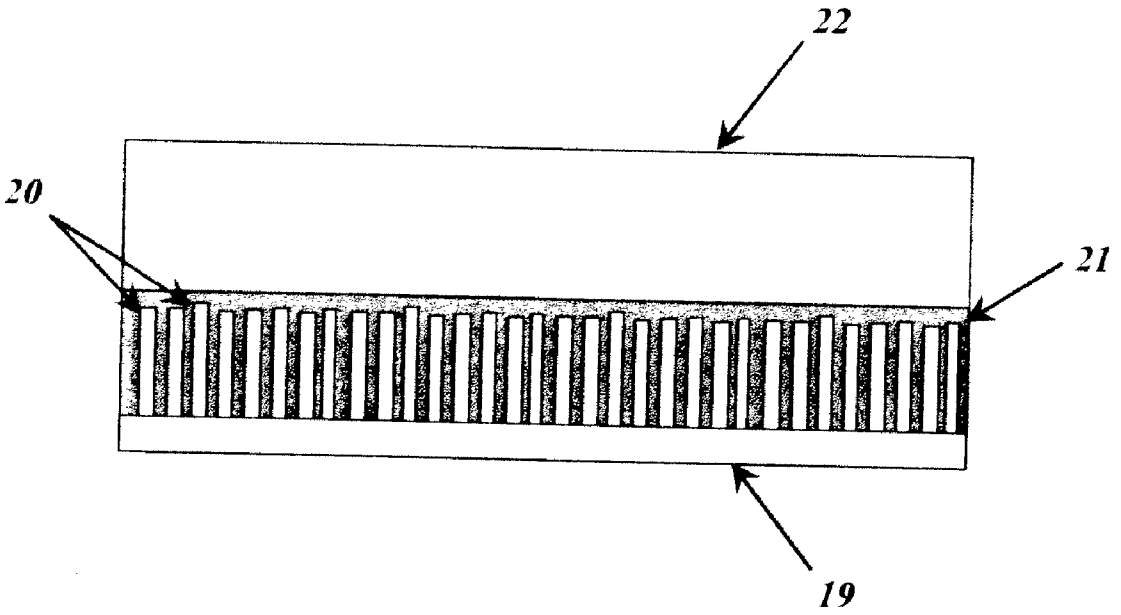

Figure 14

DIRECT ASSEMBLY PROCESS FOR FABRICATION OF IONOMERIC POLYMER DEVICES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Patent Application Ser. No. 60/661,015 filed Mar. 14, 2005, and the complete contents of this application are herein incorporated by reference.

STATEMENT OF GOVERNMENT INTEREST

[0002] This invention was made with government support under Contract Number DAAD19-02-1-0275 awarded by the U.S. Army Research Laboratory and the U.S. Army Research Office. The Government has certain rights in the invention.

DESCRIPTION

Background of the Invention

[0003] 1. Field of the Invention

[0004] The present invention generally relates to ionic polymer transducers, sensors and actuators.

[0005] 2. Description of the Prior Art

[0006] Ionomeric polymer membranes are materials that behave as solid-state electrolytes, making them useful in a variety of applications, including fuel cells, water electrolyzers, transducers, actuators and sensors. Ionomeric polymer membrane transducers have existed in their current state since the early 1990s. See, for example, Sadeghipour, K., Salomon, R., and Neogi, S., 1992, "Development of a Novel Electrochemically Active Membrane and 'Smart' Material Based Vibration Sensor/Damper."*Smart Materials and Structures,* 1, pp. 172-179 and U.S. Pat. No. 5,268,082 to Oguro, U.S. Pat. No. 6,109,852 to Shahinpoor and Mehran, and U.S. Pat. No. 6,475,639 to Shahinpoor and Mehran, each of which are herein incorporated by reference.

[0007] These devices are composed of ionomer membranes that are coated on each side with a conductive electrode. The most often used ionomer is Nafion. Nafion consists of a perfluorinated Teflon-like backbone chain and has pendant side chains that are terminated in sulfonate exchange sites. Each sulfonate exchange site has an associated cation. The presence of these charged groups allows the polymer membrane to conduct ions and thus serve as a polymer electrolyte. This property also allows the polymer membrane to behave as a distributed actuator or sensor due to the redistribution of the ions within the polymer under the application of an electric field or when a stress is applied to the membrane.

[0008] An ionomeric polymer membrane transducer can be made to bend when a small voltage (1-5 V) is applied across its thickness, thus making it a soft, distributed actuator Ionomeric polymer membrane actuators have several advantages over other types of actuation technology. For example, they are soft and therefore are compatible with compliant structures and biological tissues. Also, as compared to many other types of smart materials, these actuators generate larger strains (>10% is possible) at lower applied electric fields (1-100 kV/m).

[0009] These membranes can also be used as distributed sensors—the transient voltage generated across the membrane has been correlated to the quasi-static displacement of the membrane (see for example Shahinpoor, M.; Bar-Cohen, Y.; Simpson, J.; and Smith, J., **1998**, "Ionic Polymer-Metal Composites (IPMCs) as Biomimetic Sensors, Actuators and Artificial Muscles—a Review,"*Smart Materials and Structures,* 7, pp. R15-R30). Newbury and Leo have shown that the charge generated at the surfaces of the membrane is proportional to the strain in the material (see, Newbury, K. and Leo, D. J., 2002, "Electromechanical Modeling and Characterization of Ionic Polymer Benders."*Journal of intelligent Material Systems and Structures,* 13(1), pp. 51-60).

[0010] In order for this transduction to occur, two conditions must be met. First, the cations must be free to move about within the polymer matrix. This is typically accomplished by saturating the polymer with a diluent. U.S. Pat. No. 5,268,082, to Oguro discloses an actuator element based on a water-swollen ionomer membrane that is coated with conductive electrodes composed of a noble metal. Also disclosed are actuators swollen with salt water and physiological salt water. However, these actuators are unable to operate in air without a means of supplying continuous hydration due to drying of the device by evaporation of the water.

[0011] U.S. Pat. No. 6,109,852, to Shahinpoor and Mehran discloses a method for forming electrodes on ionomeric membranes by electroless plating. In this method, the ion exchange properties of the polymer are used to facilitate the deposition of the metal. The polymer is pretreated by roughening, hydrating, and cleaning in acid. The membrane is then placed into an aqueous solution containing ions of the metal to be plated. For example, an aqueous solution of tetraammineplatinum chloride is often used for the deposition of platinum metal into the membrane. Ions within the solution are allowed to exchange with the cations in the polymer for a predetermined amount of time. The membrane is then soaked in a solution of a reducing agent (typically $NaBH_4$ or $LiBH_4$). This process results in the reduction of the absorbed ions to their neutral state at and just below the surface of the polymer. This procedure for plating ionomer membranes with metal is typically called "impregnation/reduction" or "exchange/reduction." This method is followed by a second electroless plating in which further metal is deposited on the surface of the device.

[0012] U.S. Pat. No. 6,475,639, to Shahinpoor and Mehran discloses sensors and actuators composed of an ion exchange polymer with attached embedded electrodes and encapsulated within an impermeable coating. The embedded electrodes are formed by electroless plating of platinum as disclosed in U.S. Pat. No. 6,109,852 to Shahinpoor and Mehran. These sensors and actuators are operated in their water-swollen state and an impermeable coating such as latex is disclosed for containing the water within the polymer. By thus trapping the water within the polymer, it is proposed that the devices may be operated in air.

[0013] U.S. patent application Ser. No. 10/921,347 to Bennett et al. discloses the use of ionic liquids as diluents for ionomeric polymer transducers, actuators, and sensors to replace water. Ionic liquids have immeasurably low vapor pressure and therefore will not evaporate when the devices

are operated in air. Ionic liquid-swollen transducers are demonstrated to have lifetimes of more than 250,000 cycles when operated in air as compared to a lifetime of only 3000 cycles for a comparable water-swollen transducer. This patent application also discloses the use of a modified impregnation/reduction method for forming the electrodes on these devices. This modified method utilizes an alcohol added to the metal salt and reducing agent solutions during the plating process. The purpose of this addition is to increase the size of the membrane during the electrode formation steps in order to reduce the tendency for electrode cracking when the transducers are dried and re-swollen with ionic liquid. In addition to the modified impregnation/reduction method, other means of depositing the electrodes are disclosed. These include spraying or brushing from a solution containing a conductive powder, a suspension of an ionomer, and possibly an ionic liquid. It is suggested that a secondary conductive metal layer be deposited on top of this electrode by sputter coating.

[0014] Kim and Shahinpoor disclose a method for forming an ionomeric polymer transducer in which one electrode is first cast by pouring a mixture containing an ion conducting powder and an electroactive polymer solution into a mold, followed by pouring an electroactive polymer solution on top of this electrode (Kim, K. and Shahinpoor, M., 2002, "A Novel Method of Manufacturing Three-Dimensional Ionic Polymer Metal Composites (IPMCs) Biomimetic Sensors, Actuators, and Artificial Muscles,"*Polymer,* 43, pp. 797-802). A second electrode is formed in like manner to the first. Each layer is dried before adding the next layer. Also, the authors indicate that further enhancement of the surface conductivity may be accomplished by electroplating or electroless plating. Although this process is not demonstrated in practice, it may well be suitable for fabricating ionomeric transducers. However, the authors make no mention of the diluent to be used in the transducers and it is left to the reader to assume that the final device will be swollen with water. The authors also erroneously refer to the metal particles as an "ion conducting powder," when they are in fact electron conductors. It should also be pointed out that the authors do not mention the use of high surface area powders in the electrodes. Although transducers fabricated using this technique are not demonstrated, the authors do demonstrate actuators that are formed by casting an ionomer membrane from solution followed by plating with platinum using the impregnation/reduction process. These actuators are tested in their water-swollen state. They indicate that the cast ionomer membranes must be annealed at high temperature in order to induce crystallinity in the polymer and thus make it water insoluble. No method of adhering the cast layers together is discussed.

[0015] Shahinpoor and Kim have also disclosed a method for forming the electrodes through physical loading (Shahinpoor, M. and Kim, K., 2001, "Novel Physically Loaded and Interlocked Electrode Developed for Ionic Polymer-Metal Composites (IPMC's)," In *Electroactive Polymer Actuators and Devices*, Proceedings of the SPIE, vol. 4329, pp. 174-181). In this technique, a metal powder is suspended in a mixture of volatile solvents. The suspension is sprayed or brushed onto a backing sheet several times to create a dispersed powder layer. This backing sheet is then pressed onto an ionomer membrane, thus forcing the metal particles into the membrane to a small depth. Following this treatment, additional metal is applied using the impregnation/reduction method. This physical loading method is less expensive than the impregnation/reduction method and could be used to incorporate silver, graphite and palladium particles in the membrane. Physically loading the membrane reduces the number of impregnation/layers required from an average of 5 to 1.

[0016] In 2001, Taegeun et al. developed a replication method to manufacture a large surface-area ionic polymer actuators (Noh, T.; Tak, Y. S.; Nam, J.; Jeon, J.; Kim, H.; Choi, H.; Bae, S. S., 2001 "Development of Large-Surface Nafion-Metal Composite Actuator and Its Electrochemical Characterization," In *Electroactive Polymer Actuators and Devices*, Proceedings of the SPIE, vol. 4329, pp. 458-465). In this method, Nafion films were cast from solution onto high surface area etched aluminum foil templates. The films were then removed from the aluminum templates and platinum electrodes were formed by the impregnation/reduction process. This method increased the polymer/metal interfacial area beyond that possible without the use of a high surface area template and resulted in a transducer with superior actuation properties.

[0017] The platinum electrodes that are formed by the impregnation/reduction technique typically penetrate into the membrane to a depth of 5-30 microns. It has been shown in both experiment and theory that this penetration strongly influences transducer performance. Oguro et al. have shown that the generated strain per unit input voltage is increased by increasing number of platinum layers plated on the membrane until the mechanical stiffness of the electrode reduces the deflection (Oguro, K.; Fujiwara, N.; Asaka, K.; Onishi, K. and Sewa, S., 1999, "Polymer Electrolyte Actuator with Gold Electrodes," In *Electroactive Polymer Actuators and Devices*, Proceedings of the SPIE, vol. 3669, pp. 64-71). This is because the penetration depth of the metal is increased by performing the impregnation/reduction process repeatedly. As the penetration depth of the metal is increased, the interfacial area between the ionomeric polymer and the metal is increased. It has been shown that actuation in ionomer transducers is directly related to the accumulation of charge at the polymer/metal interface (see Nemat-Nasser, S., 2002, "Micromechanics of Actuation of Ionic Polymer-Metal Composites,"*Journal of Applied Physics,* 92, pp. 2899-2915). Furthermore, Akle et al. have correlated the actuation properties of the transducers with their capacitance (Akle, B. J.; Leo, D. J.; Hickner, M. A.; and McGrath, J. E., 2005, "Correlation of Capacitance and Actuation in Ionomeric Transducers,"*Journal of Materials Science,* 40, pp. 1-10). This result was consistent for different ionomers with substantial differences in structure and composition. Therefore it strongly supports the claim that charge accumulation at the polymer/metal interface is a major factor controlling the strain generation behavior of the actuators. Furthermore, the strain rate is determined by the speed with which the charge may be accumulated. This experimental result is supported by physics-based modeling efforts that highlight the role played by the boundary layer that forms at the interface of the electrode and the polymer (see for example Leo, D. J.; Wallmersperger, T.; and Farinholt, K., 2005, "Computational Model of Ionic Transport and Electromechanical Transduction in Ionomeric Transducers," In *Electroactive Polymer Actuators and Devices*, Proceedings of the SPIE, vol. 5759, pp. 170-181). Based on these understandings, the performance of ionomeric polymer transducers is fundamentally limited by the volume of

charge that can be accumulated at the ionomer/electrode interface and the rate with which this charge can be accumulated.

SUMMARY OF THE INVENTION

[0018] It is therefore an object of the present invention to provide a new fabrication technique for ionomeric transducers, actuators and/or sensors using a more precise, more controllable, and less expensive method. The transducers of the invention exhibit superior transduction performance, including larger strain generation. This method allows the area of the ionomer/electrode interface to be maximized and the geometry and morphology of the electrode and the ionomer/electrode interface to be well-controlled. Additionally, this invention includes a technique to ensure that the electrical conductivity of the electrodes in the plane of the transducers is high.

[0019] According to the invention, a novel fabrication technique for ionomeric polymer transducers named the direct assembly process (DAP) was developed. The DAP method allows the use of any type of ionomer, diluent, and conducting powder in the transducer, and permits the exploration of any novel ionomer design. Several conducting materials have been incorporated in the electrode along with other high surface area conductive materials to optimize the peak strain and strain rate in the actuator. Materials studied are hydrous and anhydrous ruthenium (IV) oxide (RuO_2), single walled carbon nanotubes (SWNT), gold flakes, high surface area carbon black, and platinum. The maximum strain generated at the outer surface of the transducers of the invention was on the order of 5%, and the maximum strain rate was approximately 1%/s.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] **FIG. 1** is a generalized schematic of an ionomeric polymer sensor.

[0021] **FIG. 2** is a generalized schematic of an ionomeric polymer actuator.

[0022] **FIG. 3** is a generalized schematic of an ionomeric polymer transducer.

[0023] **FIG. 4** is an illustration of the relative position of the seven layers of the device of the invention, when seven layers are used.

[0024] **FIG. 5** is an illustration of the relative position of the five layers of the device of the invention, when five layers are used.

[0025] **FIG. 6** is a flow chart describing one embodiment of the invention wherein mixed ionomer/conductor layers are formed on an ionomeric polymer membrane that is not swollen with a diluent.

[0026] **FIG. 7** is a flow chart describing one embodiment of the invention wherein mixed ionomer/conductor layers are formed on an ionomeric polymer membrane that is not swollen with a diluent followed by swelling the device with water.

[0027] **FIG. 8** is a flow chart describing one embodiment of the invention wherein mixed ionomer/conductor layers are formed on an ionomeric polymer membrane that is swollen with a diluent.

[0028] **FIG. 9** is a flow chart describing one embodiment of the invention wherein mixed ionomer/conductor/diluent layers are formed on an ionomeric polymer membrane that is swollen with a diluent.

[0029] **FIG. 10** is a schematic of a nanowire array attached to an electronically conducting layer.

[0030] **FIG. 11** is a flow chart describing one embodiment of this invention wherein mixed ionomer/conductor/diluent layers are formed on electronically conducting layers and hot pressed onto an ionomer membrane that is swollen with a diluent.

[0031] **FIG. 12** is a schematic of a nanowire array with a mixed ionomer/conductor/diluent layer deposited onto the array such that it covers the nanowires and fills the spaces between them.

[0032] **FIG. 13** is a flow chart describing one embodiment of this invention wherein mixed ionomer/conductor/diluent layers are formed on electronically conducting layers followed by forming ionomer/diluent layers and then attaching at least two such layups by hot pressing.

[0033] **FIG. 14** is a schematic showing a mixed ionomer/conductor/diluent layer deposited onto a nanowire array and covered with an ionomer/diluent layer.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

[0034] This invention contemplates the development of a new fabrication method for ionomeric polymer transducers, called the "direct assembly process" or "direct assembly method." The direct assembly method is inspired by fabrication techniques used in preparing hydrogen fuel cells. The electrodes formed by the methods of this invention are composed of two parts: a first electrode layer having a high ionomer/conductor interfacial area onto an ionomer membrane and a second electrode layer having a high electrical conductivity. There are three main embodiments of this invention. The first two embodiments involve forming the first electrode layer on an ionomer membrane that is either dry or swollen with a diluent followed by forming the second electrode layer. In both of these embodiments, the first electrode layer can be either deposited directly onto the membrane or deposited separately onto a decal and later hot pressed on to the membrane. In the third embodiment, the first electrode layer is formed directly on the second, electrically conductive layer and then the assembled layers are attached to an ionomer membrane that is swollen with a diluent.

[0035] Ionomeric polymer transducers have most commonly been fabricated using the perfluorosulfonate ionomer Nafion. However, any ionomeric polymer may be used to fabricate an ionomeric polymer transducer. Besides Nafion, some examples of other appropriate ionomers are: perfluorocarboxylate membranes, sulfonated poly(arylene ether sulfone), sulfonated poly(arylene thioether sulfone), sulfonated poly(ether ketone ketone), sulfonated polystyrene, and sulfonated polybutadiene.

[0036] Ionomers are polymers that contain a small but significant content of ionic or ionizable groups. Typically, ionomers contain an ionic group that is covalently bonded to

the polymer backbone. This bonded ionic group has an associated counterion that is not covalently bonded to the polymer backbone. Ionomer membranes are also sometimes called ion exchange membranes and fall into the categories of anion exchange membranes and cation exchange membranes. In the case of anion exchange membranes, the ionic group bonded to the polymer is a cation, for example NH_3^+, NH_2^+, N^+ and the counterion is an anion. In the case of cation exchange membranes, the ionic group bonded to the polymer is an anion, for example $COOH^-$, SO_3^-, and the counterion is a cation. Nafion is a cation exchange ionomer.

[0037] This invention describes a process for forming electrodes on ionomeric polymer membranes for the purpose of creating ionomeric polymer sensors, actuators, or transducers. The generalized form of an ionomeric polymer sensor is shown in **FIG. 1**. An ionomeric polymer sensors consists of an ionomeric device **1**, connected to electrical wires, leads, contacts, or connections **2** that are electrically connected to the electrodes on each side of the ionomeric device. Motion, strain, or stress generated in the ionomeric device **1** by an external mechanical stimulus will generate a signal that can be measured by at the electrical contacts **2**. The form of the ionomeric device could be a beam, diaphragm, strip, sheet, plate, tube, etc. and the form of the mechanical input could be strain or stress resulting from shear, bending, elongation, torsion, twisting, compression, etc. of the ionomeric device. The form of the signal measured from the ionomeric sensor could be voltage, charge, or current.

[0038] The generalized form of an ionomeric polymer actuator is shown in **FIG. 2**. An ionomeric polymer sensor comprises an ionomeric device **3**, connected to electrical wires, leads, contacts, or connections **4** that are electrically connected to the electrodes on each side of the ionomeric device. An external electrical stimulus delivered to the ionomeric device **3** by the electrical connections **4** will generate motion, stress, or strain of the ionomeric device. The form of the ionomeric device could be a beam, diaphragm, strip, sheet, plate, tube, etc. and the form of the motion generated could be strain or stress in the form of shear, bending, elongation, torsion, twisting, compression, etc. of the ionomeric device. The form of the electrical stimulus could be voltage, charge, or current.

[0039] An ionomeric polymer transducer is a generalized form of an ionomeric polymer sensor or actuator. A transducer refers to a device that can be used either as a sensor or an actuator. As shown in **FIG. 3**, an ionomeric polymer transducer consists of an ionomeric polymer device **5** with electrical contacts, leads, wires, or connections **6** that make electrical contact to the electrodes on the ionomeric polymer device. The ionomeric polymer device can be deformed by an external mechanical input such as motion, strain or stress resulting from shear, bending, elongation, torsion, twisting, compression, etc. and will generate a signal such as voltage, charge, or current that can be measured at the electrical connections **6**. Likewise, the transducer can be excited by an electrical stimulus such as voltage, charge, or current delivered to the electrical contacts **6**. This will result in motion, stress, or strain of the ionomeric polymer device such as shear, bending, elongation, torsion, twisting, compression, etc. The form of the ionomeric polymer device **5** could be a beam, diaphragm, strip, sheet, plate, tube, etc.

[0040] The electrodes formed by the methods of this invention are comprised of two parts: a mixed layer that contains some ionomeric polymer and particles of an electronically conductive material, and a surface layer that only contains electronically conductive material. In practice, an ionomeric polymer transducer fabricated by the techniques described in this invention would be composed of, for example, seven or five layers, as shown in **FIGS. 4 and 5**. For the exemplary device composed of seven layers (**FIG. 4**), the outermost layers **7** have a high electrical conductivity and may be connected to the other layers by means of a binder layer **8**, the next inner layers **9** possess a high ionomer/conductor interfacial area, and the central layer **10** is composed only of ionomeric polymer and diluent. For the exemplary device composed of five layers (**FIG. 5**), the outermost layers **11** have a high electrical conductivity, the next inner layers **12** have a high ionomer/conductor interfacial area, and the central layer **13** is composed only of ionomeric polymer and diluent.

[0041] One innovation of this invention is a technique for forming the mixed ionomer/conductor layers **9** and **12** of the described electrodes. This technique is carried out as follows. First, a liquid suspension of an ionomer is created. Although Nafion polymer cannot be dissolved in the true sense of the word, Grot has described a process for creating suspensions of Nafion polymer in mixed solvents of water and various alcohols (U.S. Pat. No. 4,433,082 which is herein incorporated by reference). Liquid compositions of other ionomers besides Nafion could be used. Examples of other ionomers which may be used for the present invention include but are not limited to: perfluorocarboxylate ionomers, sulfonated poly(arylene ether sulfone), sulfonated poly(arylene thioether sulfone), sulfonated poly(ether ketone ketone), sulfonated polystyrene, and sulfonated polybutadiene. Liquid suspensions of ionomers other than Nafion can be formed by those of skill in the art. Also, liquid suspensions of Nafion polymer are commercially available. The next step in the process involves of adding a powder of an electronically conductive material to the polymer solution. Any electronically conductive powder may be used. The properties of the powder may be altered and tailored in order to modify or improve the transduction behavior of the resulting device. Examples of electronically conductive material that could be used are metals as gold, silver, copper, nickel, etc. or conductive polymers or carbon nanotubes. The form of the powder particles could be spheres, rods, tubes, flakes, etc. Metal oxides such as ruthenium (IV) oxide may also be used. It is desired that the conductive powder possess a high surface area and a high electrical conductivity. Additional solvents may also be added to the ionomer/conductor mixture in order to enhance dispersion of the conductive particles. This may be especially important when using electronically conductive powders such as carbon nanotubes and for high loading of the electronically conductive powder. One such additional solvent is isopropyl alcohol (IPA). Other alcohols or appropriate solvents may also be used, provided that they are miscible with the ionomer/conductor mixture and readily removed by evaporation. Glycerol or another appropriate material may also be added to the mixture in order to adjust the viscosity for the specific application procedure (brushing, spraying, etc.)

[0042] It is important for the mixture be uniform so that the electrode layers made from the mixture will be homogenous and the properties of the resulting sensor, actuator, or

transducer will be uniform throughout. In order to throroughly disperse the particles of the electronically conductive powder, the mixture is preferably sonicated for an extended period of time. This can be accomplished by positioning the ionomer/conductor/solvent mixture within a sealed jar. The jar may then be positioned in an ultrasonic bath, typically containing water. The level of water should at least be as high as the level of the mixture within the jar. The mixture should also be stirred in order to prevent settling of the particles. This can be accomplished by shaking the jar or by using a magnetic stirring plate. During the sonication step, the mixture should be stirred at intervals of approximately 30 minutes for periods of approximately 5 minutes. The mixture should be sonicated and stirred for typically 1 to 6 hours to ensure homogeneity and full dispersion of the metal particles. The necessary duration of mixing and sonication depends on the type of conducting powder, the concentration of polymer solution, and the loading of conductive powder. In some cases, such as when carbon nanotubes are to be used, sonication for up to 12 hours may be necessary.

[0043] Once the mixture has been sufficiently stirred and sonicated (or a generally uniform dispersion is formed by other means) so as to completely disperse the electronically conductive particles, it may be applied to the membrane or to a decal by a variety of methods. The ionomeric polymer of which the membrane is comprised and the ionomeric polymer within the liquid mixture need not be the same. Prior to the deposition of the ionomer/conductor layer, the substrate ionomer membrane may be prepared by pretreating. Alternatively, the ionomer membrane may be used in its as-received form. This pretreating may involve roughening of the membrane by sanding, washing of the membrane by boiling in acid, and ion-exchange of the membrane by soaking in an aqueous salt solution. The roughening step is carried out by sanding the dry membrane with 600-grit sandpaper in a 90-degree cross-hatching pattern) on both sides. The membrane may then be washed by boiling in 1.0 M sulfuric acid for 30-60 minutes followed by boiling in de-ionized water for 30-60 minutes. The membrane at this point will be in the hydrogen ion form. The hydrogen ion may be exchanged for another ion by soaking the membrane in a concentrated (>0.5 M) solution of a salt of the ion to be exchanged. Yeager and Steck have shown that the counterions of Nafion may be exchanged for any cation by soaking the hydrated membrane in an aqueous solution of the chloride salt of that ion (see Yeager, H. L. and Steck, A., 1979, "Ion-Exchange Selectivity and Metal Ion Separations with a Perfluorinated Cation Exchange Polymer,"*Analytical Chemistry,* 51, pp. 862-865). Following the pretreatment, the membrane should be dried prior to deposition of the ionomer/conductor layer. This drying may be carried out by baking the membrane at 80-150 degrees Centigrade under vacuum for 3-12 hours.

[0044] In one embodiment of this invention, the ionomer/conductor layer is deposited directly onto the thus prepared ionomer membrane immediately following the drying step. The process flow for this method is depicted in **FIG. 6** beginning with step **101**. In this embodiment, the ionomer membrane does not contain a diluent. The deposition of the ionomer/conductor layer may be carried out by any of several methods. In the first method, the mixture may be painted onto the membrane using a brush. In this method, a thin layer of the mixture should be applied by brushing in a single direction across the membrane surface. The membrane should be properly constrained during the painting step to prevent wrinkling of the membrane caused by absorption of the solvents present in the ionomer/conductor/solvent mixture. Following the deposition of the first layer by brushing, the solvents should be removed from the painted layer by heat, vacuum, or a combination of heat and vacuum. If glycerol has been added to the ionomer/conductor mixture in order to increase its viscosity, then the solvents may be removed by heating at 130 degrees Centigrade under vacuum for 15 minutes. If glycerol has not been added and only more volatile water and alcohols are present, then lower temperature, less time and/or less or no vacuum may be sufficient to dry the painted layer. Care should be taken to avoid unnecessarily rapid drying of the layer or cracking may result. Additionally, dimethyl sulfoxide, dimethyl formamide, or ethylene glycol may be added to the mixture in order to improve the drying properties of the layer and reduce the tendency for cracking. Following the deposition of the first layer, a second layer should be applied by painting in a direction that is rotated by 90 degrees with respect to the direction of painting of the first layer. The purpose of rotating the direction of application of each subsequent layer is to ensure the uniformity of the electrode. This layer should be dried in a similar manner to the first layer. The ionomer/conductor mixture should be stirred and sonicated between the deposition of each layer in order to prevent settling and coagulation of the conductive particles. In order to increase the thickness of the mixed ionomer/conductive particle layer, several layers should be applied to the membrane. Good results may be obtained with as few as 1 layer, but as many as 30 may be applied. Once the layers have been applied to one side of the membrane, the membrane should be flipped over and the layers should be applied to the other side using the same procedure.

[0045] Alternatively, the mixed ionomer/conductor layers may be applied to the membrane by spraying. One way to accomplish this deposition is to spray the mixture onto the membrane surface using an airbrush. Other suitable means of spraying the mixture onto the membrane surface may also be used. As before, the layers should be dried between each successive deposition step. If the layers are deposited by spraying, then the addition of glycerol to thicken the electrode mixture may not be necessary. If glycerol is not used, then the temperature, time, and vacuum used to dry each layer should be adjusted accordingly.

[0046] In addition to brushing and spraying, other appropriate means of depositing the ionomer/conductor mixture onto the ionomer membrane in alternating layers could also be used.

[0047] After the mixed ionomer/conductive particle layers have been applied to both sides of the membrane, the layers should be adhered to the membrane by hot-pressing at step **103**. In this step **103**, the layered structure should be positioned between two protective films composed of an appropriate high temperature polymer such as Kapton (polyimide) or Teflon (polytetrafluoroethylene) and placed between the platens of a heated laminating press. The temperature used should be above the glass transition temperature of the dry ionomer and the pressure used should be sufficient to force the electrode layers and the ionomer membrane together without causing damage to the membrane. For dry Nafion membranes, a temperature of 210 degrees Centigrade and a pressure of 20 MPa is sufficient.

For other ionomers different parameters may be necessary. For example, for the dry ionomer poly(arylene ether sulfone), a temperature of 240 degrees Centigrade is required. The pressing should be carried out for a sufficient period of time, for example 2-10 minutes. The parameters for the hot pressing step will fall within the range of 5-500 MPa, 150-300 degrees Centigrade, and 1-300 minutes. It is desirable that the ion within the ionomer membrane be exchanged for an ion other than hydrogen during the pretreatment step **104**. Appropriate ions are any ion other than hydrogen, most preferably alkali metal ions such as sodium, potassium, cesium, etc. The purpose of this exchange at step **104** is to prevent damage to the ionomer membrane during the high temperature pressing step. Nafion membranes in the hydrogen ion form are known to char during processing at high temperature.

[**0048**] In another embodiment of this invention, the mixed ionomer/conductive particle layers may be deposited onto a decal that is separate from the substrate ionomer membrane. This is depicted in **FIG. 6** as the method initiating with step **102**. This decal should be composed of an appropriate high temperature polymer film and may be Kapton, Teflon, or more preferably, fiberglass-reinforced Teflon. Alternatively, metal foil could be used. In this embodiment of the invention, the ionomer/conductive particle mixture should be prepared using the same procedures described previously. The mixture should then be applied to the decals in a layered fashion using the same procedures described previously, with drying between each deposited layer. The ionomer membrane should also be prepared by pretreating as previously described. Following the deposition of the ionomer/conductor layer onto two decals, the decals should be positioned on each side of the ionomer membrane and placed between the platens of a heated laminating press. The electrode layers should be forced onto the ionomer membrane by pressing **103** as previously described. For dry Nafion, a pressure of 20 MPa at a temperature of 210 degrees Centigrade for a period of 2-10 minutes should be sufficient. The parameters for the hot pressing step **103** will fall within the range of 5-50 MPa, 200-250 degrees Centigrade, and 1-20 minutes. Following the pressing step, the assembly should be removed from the press and cooled to room temperature. The decals should then be peeled away from the membrane. The mixed ionomer/conductor layers will remain attached to the ionomer membrane.

[**0049**] Alternatively, either of the two embodiments of this invention previously described may be performed on membranes that have been swollen with a suitable diluent (step **105**). Bennett et al. has described processes for swelling ionomer membranes with ionic liquids, which can be used as stable diluents (U.S. patent application Ser. No. 10/921,347 which is herein incorporated by reference). The advantage of using an ionic liquid is that ionic liquids have high thermal stability and immeasurably low vapor pressure, so they can withstand high temperature processing. Bennett et al. has also described procedures for attaching electrodes to ionic liquid-swollen ionomer membranes by spraying or painting from a liquid containing an ionomer and electronically conductive particles. In one embodiment, the use of ionomer membranes swollen with ionic liquids and molecular (non-ionic) liquids is disclosed. These non-ionic liquids could include but are not limited to formamide, diethylene glycol, triethylene glycol, and poly(ethylene glycol). It is desirable for the diluent to possess a high enough boiling point so as to not be lost to evaporation during the hot pressing step.

[**0050**] If the process of this invention is to be carried out on an ionomer membrane swollen with a diluent, then the membrane should be swollen just after the pretreatment steps of roughening, washing, ion exchanging **104**, and drying. The swelling **105** may be performed by soaking the membrane in the diluent to be swollen at room temperature or at an elevated temperature for a period of 2-24 hours. Additionally, the diluent may be mixed with a compatible solvent such as methanol, ethanol, or n-methylformamide that readily diffuses into the ionomer membrane in order to enhance the rate of uptake of the diluent. Also, a sealed container capable of withstanding high pressure and free of leaks may be employed if the temperature used for the uptake process is higher than the boiling temperature of any of the components of the diluent mixture. The volatile solvents may be removed by evaporation following the swelling step. High temperature and/or vacuum may be used to facilitate the removal of the volatile solvents.

[**0051**] Once the membrane is swollen with a diluent, the ionomer/conductor mixed layers should be formed either directly onto the membrane or on a separate decal using the procedures described previously. The process flow for the embodiment of this invention in which the layers are formed directly on the ionomer membrane initiates with step **119** in **FIG. 8** (swelling at step **118** being performed as described above). Once the electrode layers are formed they should be attached to the membrane by hot pressing **121**. The hot pressing step **121** should be carried out as described previously. However, due to the presence of the diluent, the glass transition temperature of the ionomer will be reduced. For this reason, the temperature, pressure, and pressing time required to adhere the ionomer/conductor layers to the membrane may be reduced. The specific parameters will be a function of the chemical structure of the ionomer, the chemical structure of the diluent used, and the loading of the diluent within the ionomer membrane. Appropriate ranges for the parameters are: 100-200 degrees Centigrade, 1-100 MPa, and 10 seconds-30 minutes.

[**0052**] Additionally, the layers may be formed separately of the membrane on a decal comprised of a high temperature polymer film such as Teflon, Kapton, or fiberglass-reinforced Teflon. This process initiates with step **120** in **FIG. 8**. As with the other methods, the electrode layers should be formed by casting or in a plurality of coats by brushing, spraying, or dipping. Following the formation of the electrode layers, they should be attached to the diluent-swollen ionomer membrane by hot pressing at step **121**. Appropriate ranges for the hot pressing parameters are: 100-200 degrees Centigrade, 1-100 MPa, and 10 seconds-30 minutes.

[**0053**] For the embodiment of this invention in which the ionomer/conductor layer is applied to a membrane that has been previously swollen with a diluent, it is desirable that the diluent also be added to the ionomer/conductor layers during deposition. This can be accomplished by mixing an appropriate amount of the diluent with the liquid mixture containing the ionomer and conductive particles prior to casting, brushing, or spraying this mixture onto the swollen membrane. This process initiates with step **125** in **FIG. 9** (swelling of the membrane at step **124** being preferably

performed as described above). The diluent must have a high enough boiling point so as to not be lost to evaporation during the drying steps between the deposition of each layer. For this reason, it may be undesireable to use glycerol as a thickener if the diluent is to be added to the mixture. The other water and alcohols present in the mixture will evaporate much more readily than glycerol and thus the temperature, time, and vacuum used in the drying step may be adjusted to achieve evaporation of the highly volatile components without loss of the diluent. Alternatively, the ionomer/conductor/diluent mixture may be applied to a decal separately of the diluent-swollen ionomer membrane. This process initiates with step **126** in **FIG. 9**. The layers thus formed should be attached to the ionomer membrane by hot pressing at ste[127. Appropriate ranges for the hot pressing parameters are: 100-200 degrees Centigrade, 1-100 MPa, and 10 seconds-30 minutes.

[**0054**] In the case where the ionomer membrane is swollen with a diluent, and the diluent is also incorporated into the ionomer/conductor layers during formation, then it may not be necessary to incorporate the diluent into the layered device following the hot pressing step **127**. If such incorporation is desired, then it should be carried out as described previously, by soaking the device in the diluent at a controlled temperature for a specified period of time. Alcohols or other solvents such as n-methylformamide may be added to the diluent in order to increase the uptake of the diluent by the device. Also, a sealed container capable of withstanding high pressure and free of leaks may be employed if the temperature used for the uptake process is higher than the boiling temperature of any of the components of the diluent mixture. This will prevent the loss of the components during the incorporation step because equilibrium will be reached between the evaporation of the components and the pressure rise within the vessel. When using such a high-pressure sealed vessel, it is desirable that the free space above the top of the liquid be kept to a minimum. After the swelling step the volatile solvents (if used) should be removed by evaporation. The volatile solvent may be removed by evaporation following the swelling step. High temperature and/or vacuum may be used to facilitate the removal of the volatile solvents.

[**0055**] In the case where the ionomer membrane and ionomer/conductor layer are not incorporated with a diluent prior to and during the forming step, then a diluent may be incorporated after the forming step (**FIGS. 6 and 7**; **101**, **102**, **108**, **109**). Following the hot pressing of the mixed ionomer/conductor layers onto the membrane, the device may be processed further prior to incorporation of the diluent. This processing may include washing the device by boiling in sulfuric acid followed by boiling in deionozed water. After this step the device may be ion exchanged by soaking in a solution of a salt of the ion to be exchanged.

[**0056**] Transducers exchanged with large cations have superior performance to those exchanged smaller cations when an ionic liquid is used as the diluent. Therefore, it is preferable for the current invention that alkylammonium cations be employed as the counterion of the membrane if an ionic liquid is to be used as the diluent. Most preferably, the counterion should be tetramethylammonium, tetraethylammonium, tetrabutylammonium, or tetrapropylammonium. These cations can be exchanged into the membranes by first converting the membrane with the electrode layers attached to the hydrogen ion form by boiling in acid (e.g. 1.0 M sulfuric acid) followed by soaking for several days in a 0.5 M aqueous chloride salt of the cation to be exchanged.

[**0057**] After the ion exchange, the device should be rinsed with deionized water and dried under heat and vacuum. The device may then be swollen with an ionic liquid using the procedures described previously.

[**0058**] For all of the described embodiments, the mixed ionomer/conductor layers should contain between 10 and 90% of electronically conducting powder by volume. If a diluent is incorporated into the layers during the formation process, then the volume of the diluent should be between 5 and 150% of the volume of ionomeric polymer in the layers. The thickness of the electrodes should be between 1 and 2000 microns.

[**0059**] The electrodes formed by the processes described by this invention are composed of two parts: the mixed ionomer/conductor layer **9** and **12** and an electronically conductive surface layer **7** and **11**. The purpose of the mixed ionomer/conductor layer is to create a large interfacial area between the conductor and the ionomer. However, the mixed ionomer/conductor layer lacks sufficient electrical conductivity to allow an even voltage to be applied over the surface of an ionomeric transducer, especially if the transducer dimensions are substantially large (1-100 cm). In order to overcome this problem, a second layer is applied. The purpose of this secondary layer is only to allow current to flow in the direction parallel to the plane of the electrode—it does not contribute substantially to the conductor/ionomer interfacial area. This electronically conductive layer should always be applied after all of the steps of swelling the device with diluent have been completed.

[**0060**] For the case where the diluent is added to the membrane after the hot pressing step, water may be used as the diluent. If water is used as the diluent, then the conductive surface layers should be applied using one of the two process flows shown in **FIG. 7**. In the process flow initiating at step **111**, a thin conductive layer is applied to the dry device by sputtering (it being understood that the forming and attaching steps **108**, **109**, and **110** are preferably performed in the same manner as described above). This thin conductive layer formed in step **111** would preferably be a metal and would most preferably be a noble metal such as gold, platinum, palladium, or rhodium. The device is then swollen with water in step **113** by soaking in water at 25-100 degrees Centigrade for 10 minutes-12 hours. Additional conductive material may then be deposited on the surface or surfaces of the device by electroplating or electroless plating in step **115**. This additional conductive layer would preferably be a metal and would most preferably be a noble metal such as gold, platinum, palladium, or rhodium. The cation within the device may then be exchanged in step **117** by boiling in sulfuric acid followed by soaking in a salt of the cation to be exchanged.

[**0061**] Alternatively, the membrane could be swollen with water prior to the formation of the conductive surface layer. This method is initiated with step **112** in **FIG. 7**. In this case, a conductive material, preferably a metal, and most preferably a noble metal such as gold, platinum, palladium, or rhodium, is deposited onto the surface of the device by using the exchange/reduction method in step **114**. This method has been described by, for example Fujiwara, N.; Asaka, K.;

Nishimura, Y.; Oguro, K.; and Torikai, E., 2000, "Preparation of Gold-Solid Polymer Electrolyte Composites as Electric Stimuli-Responsive Materials,"*Chemistry of Materials,* 12, pp. 1750-1754 and Millet, P.; Durand, R.; Dartyge, E.; Tourillon, G.; and Fontaine, A., 1999, "Precipitation of Metallic Platinum into Nafion Ionomer Membranes,"*Journal of the Electrochemical Society,* 140, pp. 1373-1379. After this treatment, additional conductive material may be deposited on the surface or surfaces of the device by electroplating or electroless plating in step **116**. This additional conductive layer would preferably be a metal and would most preferably be a noble metal such as gold, platinum, palladium, or rhodium. Finally, the cation within the device may then be exchanged by boiling in sulfuric acid followed by soaking in a salt of the cation to be exchanged at step **117**.

[**0062**] In these methods, the conductive surface layer is deposited by processes in which the device is placed into aqueous solutions. For the embodiment of this invention wherein a diluent other than water is to be used, these processes are not appropriate.

[**0063**] When high boiling diluents are to be used, the conductive surface layer is formed by hot pressing a layer of gold leaf onto the surface of the device. This is depicted in **FIGS. 6, 8** and **9**. Appropriate ranges for the parameters to be used in the hot pressing step are 10 kPa-20 MPa pressure, 100-200 degrees Centigrade temperature, and 5 seconds-60 minutes time. Alternatively, in order to improve the adhesion of the gold leaf to the device, both sides of the device may be coated with a thin layer of ionomer prior to the hot pressing step (see steps **106**, **122**, and **128** in **FIGS. 6, 8** and **9** respectively). This can be accomplished by brushing or spraying from a liquid mixture containing a suspended or dissolved polymer. The concentration of the mixture should be between 1% and 40% polymer by weight. The polymer to be used as the binding layer should be an ionomer, a polyurethane, a poly(urethane urea), or a mercaptan. After a thin coating of the mixture has been brushed or sprayed onto one side of the device, it should be dried using an appropriate combination of temperature, time, and vacuum. Following the deposition of this layer on one side of the device, the process should be repeated on the opposite side.

[**0064**] After the thin binding layer has been deposited on the device, it should be positioned between two electronically conductive layers. The thickness of this electronically conductive layer may be between 10 nm and 10,000 nanometers. These layers may be for instance metal foil or metal leaf. Preferably, the electronically conductive layers should be comprised of a noble metal such as gold, platinum, palladium, or rhodium. Most preferably, the metal foil or leaf should be comprised of gold. The gold foil or leaf may be supported on a backing sheet. These layers may be positioned between two protective films composed of Kapton, Teflon, or another high temperature polymer and heated under pressure for a specified period of time as indicated in steps **107**, **123**, and **129**. Appropriate ranges for the pressing parameters are: 100-200 degrees Centigrade, 10 kPa-20 MPa, and 5 seconds-60 minutes. This pressing may be performed using a heated laminating press or by placing the device, gold leafs, and protective films below a weight in an oven. After the pressing step, the assembly should be cooled to room temperature and the backing sheets should be peeled away. The gold foil or leaf will remain attached to the ionomer device.

[**0065**] By forming electrodes in the manner described, the area of the ionomer/electrode interface may be maximized. However, the speed of the transduction mechanism may be limited by the electronic conductivity of the conducting powder that is used. This is explained as follows.

[**0066**] It is the formation of a charge double layer at the ionomer/electrode interface that gives rise to transduction in ionomeric transducers. This charge double layer is formed by ions within the electrolyte (ionomer) phase and electrons within the electronically conductive (e.g. metal) phase. Therefore, the electrode must possess a high ionic conductivity and a high electronic conductivity. However, a tradeoff exists between these two metrics. As the content of ionomer within the electrode layer is increased, the ionic conductivity of the electrode is increased, but the electronic conductivity is decreased, due to the decreased content of the electronically conductive component (e.g. metal). This tradeoff is further complicated by the fact that the high surface area materials (such as ruthenium (IV) oxide) may not possess a very high electronic conductivity, as compared to a pure metal such as gold or silver. The electronic conductivity of the electrode can be increased by adding a metal powder such as gold, but the content of the high surface area material is then reduced. Also, because the highly conductive particles are dispersed, a large number of them are required in order to increase the electronic conductivity of the electrode layer substantially.

[**0067**] The electronic conductivity along the surface of the electrodes is enhanced by the use of a metal foil. Because the foil is continuous, it may be very thin and still maintain a high conductivity. A similar approach may be employed to increase the electronic conductivity through the thickness of the electrode layers. For this reason, another preferred embodiment of this invention involves the use of an array of nanowires to simultaneously enhance the electronic conductivity in the planar direction of the transducers and through the thickness direction of the mixed ionomer/conductor layer. A schematic of a nanowire array is shown in **FIG. 10**. In this figure the nanowires **15** are shown as attached to an electronically conductive layer **14**. The diameter of the nanowires may be in the range 10-10,000 nanometers and the length of the nanowires may be in the range 1-1000 microns. The thickness of the electronically conductive layer may be in the range 10-10,00 nanometers.

[**0068**] Several researchers have reported on the synthesis of nanowire arrays using the template method (see for example Scholnenberger, C.; van der Zande, B. M. I.; Fokkink, L. G. J.; Henny, M.; Schmid, C.; Krulger, M.; Bachtold, A.; Huber, R.; Birk, H.; and Staufer, U., 1997, "Template Synthesis of Nanowires in Porous Polycarbonate Membranes: Electrochemistry and Morphology,"*Journal of Physical Chemistry B,* 101, pp. 5497-5505, and Hulteen, J. C.; and Martin, C. R., 1997, "A General Template-Based Method for the Preparation of Nanomaterials,"*Journal of Materials Chemistry,* 7, 1075-1087). In this method, a porous template such as porous alumina or ion track etched polycarbonate is used. These templates are used because they have pores that are roughly cylindrical in nature, are well-ordered, and have a narrow range of pore sizes. Fur-

thermore, the size of the pores can be controlled by the manufacturing technique and the pore density is high.

[0069] Using the template method, nanowire arrays can be fabricated from a wide variety of materials. These include metals such as copper, silver, nickel, and gold, conducting polymers such as polypyrrole and polyaniline, and other materials such as carbon and carbon nanotubes. In order to create a nanowire array, a first layer of electronically conducting material (such as metal) is deposited onto one side of the porous template using an appropriate technique. Sputtering or evaporation are common methods for the deposition of this first layer. The thickness of this first layer can be increased by electroplating or electroless plating. This first layer is then used as the cathode to perform electroplating through the pores of the template. By varying the diameter of the pores and the thickness of the template, the aspect ratio of the nanowires can be altered. The electrochemical deposition of the nanowires can be carried out using a variety of approaches, but the best results will be achieved by the use of pulse plating. Pulse plating is an electroplating technique in which a DC current is continuously switched on and off. Pulse plating is used for achieving uniform growth when plating into small holes. Pulse reverse plating may also be used.

[0070] A suitable procedure for creating the nanowire array is as follows. Other methods may be used. A ion track etched polycarbonate membrane (or other appropriate template) should be loaded into the chamber of a sputter coater. A thin layer of gold (or another metal) should be deposited onto one side of the membrane. The metal layer should be thick enough to provide sufficient electronic conductivity for electroplating. The membrane should then be attached to a mount and electrical contact should be made to the sputtered surface with a wire. The sample mount should be positioned within a gold electroplating bath and a layer of gold should be deposited onto the sputtered side of the membrane. The sample holder should then be removed from the bath and the membrane should be dismounted and inverted. Electrical contact should be made with the gold coated side using a wire. The sample mount should be repositioned within the bath and the pores should be filled with gold (or another metal) by electroplating, most preferably pulse plating or pulse reverse plating. The sample mount should then be removed from the bath and the membrane dismounted. The template should then be removed by dissolving in an appropriate solution. For the porous alumina templates this could be for example aqueous sodium hydroxide. For the ion track etched polycarbonate templates it could be an appropriate organic solvent.

[0071] The nanowire array thus formed will serve as a scaffolding on which to build the mixed ionomer/conductor layer. The electronically conductive layer **14** that acts at the support for the nanowires will provide high electronic conductivity in the direction planar to the transducer, thus replacing the electronically conductive layer **7** and **11**. The nanowires **9** will provide high electronic conductivity through the thickness of the electrodes, thus enabling electrons to reach the high surface area particles more rapidly and increasing the transduction speed of the ionomeric transducers. Also, due to the intimate contact between the nanowire array and the mixed ionomer/conductor layer, the adhesion of the ionomer/conductor layer to the electronically conducting layer will be excellent, and the need for a binding layer will be precluded.

[0072] After the template has been dissolved, the nanowire array should be cleaned and dried and the mixed ionomer/conductor layer should be deposited. Alternatively, this process could be performed by depositing the ionomer/conductor/diluent mixture onto a flat electronically conductive layer. This flat layer could be a foil or leaf of a metal, preferably a noble metal and most preferably gold. The process flow for this method is depicted in **FIG. 11**. The mixed ionomer/conductor layer should be deposited as described previously, by using a mixture containing a solution or suspension of an ionomer and dispersed electronically conducting particles. The ionomeric polymer within the mixture could be Nafion, perfluorocarboxylate ionomers, sulfonated poly(arylene ether sulfone), sulfonated poly(arylene thioether sulfone), sulfonated poly(ether ketone ketone), sulfonated polystyrene, and sulfonated polybutadiene.

[0073] In order to improve the performance of the transducers, the counterion within the ionomer should be exchanged for a large cation prior to the realization of the ionomer suspension or solution. This can be accomplished by boiling the ionomer in an acid (e.g. 1.0 M sulfuric acid) followed by soaking for several days in a 0.5 M aqueous chloride salt of the cation to be exchanged. Most preferably, the counterion should be tetramethylammonium, tetraethylammonium, tetrabutylammonium, or tetrapropylammonium. The ionomeric polymer should then be rinsed with deionized water. The ionomeric polymer can then be suspended or dissolved in a solvent or mixture of solvents in order to make a liquid by using a method such as that described by Grot (U.S. Pat. No. 4,433,082). Alternatively, a commercially available liquid ionomer mixture may be used.

[0074] The particles should be preferably ruthenium (IV) oxide, carbon nanotubes, conducting polymer, or another material that possesses a high surface area. Carbon or graphite powder may also be used. Additionally, the ionomer/conductor mixture should also contain a diluent. This diluent could be an ionic liquid or a non-ionic high boiling organic solvent. Suitable organic solvents are for example formamide, ethylene glycol, diethylene glycol, triethylene glycol, and poly(ethylene glycol). A suitable ionic liquid is for example 1-ethyl-3-methylimidazolium trifluoromethanesulfonate. The ionomeric polymer/conductive particles/diluent mixture should be thoroughly stirred and sonicated in order to completely disperse the conductive particles. This stirring and sonicating step should be performed for 1-6 hours as required to obtain a completely homogeneous mixture. This will ensure that the electrode layers are uniform and the properties of the resulting sensor, actuator, or transducer will be the same throughout.

[0075] Once the ionomer/conductor/diluent mixture is homogenized, it should be applied to the nanowire side of the nanowire array by spraying, bushing, casting, or another suitable means. The amount of mixture deposited should be sufficient to at least reach the top of the nanowires after the volatile components are removed. A cross-sectional view of the nanowire array with the ionomer/conductor/diluent layer in place is shown in **FIG. 12**. The nanowires **17** are connected to the electronically conductive layer **16** and the

space between the nanowires is filled by the ionomer/conductor/diluent layer **18**. The thickness of the mixed layer **18** should be at least as large as the length of the nanowires **17**. As can be seen, the ionomer/conductor/diluent layer should fill the space between the nanowires. Once the mixture is deposited, the assembly may be shaken or vibrated in order to remove trapped air and the volatile components should be removed by evaporation. Heat and/or vacuum may also be used to control the rate of drying. After the electrode is fabricated, it may be desirable to anneal the assembly in order to induce crystallinity in the ionomer. Appropriate annealing can be performed at 50-150 degrees Centigrade for 1-12 hours followed by slow cooling to room temperature.

[**0076**] Once two such electrodes are formed, an ionomeric transducer can be fabricated by hot pressing the two layers onto a diluent-swollen ionomer membrane. The ionomer membrane should be pretreated and swollen with a suitable diluent using the methods described previously. The diluent used can be an ionic liquid or a high boiling molecular liquid. The electrodes should be positioned on each side of the ionomer membrane with the ionomer/conductor side facing the membrane. The assembly should be adhered by hot pressing. Appropriate ranges for the hot pressing parameters are 1-100 MPa, 100-200 degrees Centigrade, and 10 seconds-30 minutes.

[**0077**] Once the ionomer/conductor layers have been deposited on the electronically conducting layer or nanowire array, an alternative means of forming the ionomer/diluent layer in the center of the device is available. This alternative is to deposit a second layer containing only ionomeric polymer and diluent on top of the ionomer/conductor/diluent layer.

[**0078**] The process flow for this method is depicted in **FIG. 13**. A schematic of a layup prepared using this technique is shown in **FIG. 14**. In this embodiment, the nanowires **20** are attached to an electronically conducting layer **19**. The mixed ionomer/conductor/diluent layer **21** is deposited by brushing, spraying, or casting in step **135** preferably using the procedures described above (as noted above, the ionomer membrane can be swollen with a diluent in step **134**). The ionomer/conductor/diluent layer should fill the space between the nanowires. These layers may be annealed at elevated temperature in order to induce crystallinity in the ionomer (step **136**). Appropriate annealing can be performed at 50-150 degrees Centigrade for 1-12 hours followed by slow cooling to room temperature. A layer comprised of ionomer and diluent **22** is then deposited directly onto the formed electrode layers in step **137**. This can be accomplished by spraying, brushing, or casting from a mixture containing a solution or suspension of an ionomer and a diluent.

[**0079**] This ionomer and diluent mixture should be prepared as described previously, where an ionomeric polymer is pretreated by boiling in acid (e.g. 1.0 M sulfuric acid) followed by soaking in an aqueous chloride salt solution. The counterion of the membrane will preferably be a large cation such as tetramethylammonium, tetraethylammonium, tetrabutylammonium, or tetrapropylammonium. The ionomeric polymer should then be rinsed with deionized water. The ionomeric polymer can then be suspended or dissolved in a solvent or mixture of solvents in order to make a liquid by using a method such as that described by Grot (U.S. Pat. No. 4,433,082). Alternatively, a commercially available liquid ionomer mixture may be used.

[**0080**] A diluent should then be added to the liquid ionomer mixture. This diluent could be an ionic liquid or a non-ionic high boiling organic solvent. Suitable organic solvents are for example formamide, ethylene glycol, diethylene glycol, triethylene glycol, and poly(ethylene glycol). A suitable ionic liquid is for example 1-ethyl-3-methylimidazolium trifluoromethanesulfonate. The mixture containing the ionomeric polymer and the diluent should be applied to the electrode layers **21** by casting or by brushing or spraying in a plurality of layers.

[**0081**] Once the ionomer/diluent layer is deposited onto the ionomer/conductor side of at least two electrode assemblies, the volatile components should be removed by evaporation. Afterwards, it may be beneficial to anneal the devices at high temperature in order to create crystallinity in the ionomer/diluent layers at step **138**. Appropriate annealing can be performed at 50-150 degrees Centigrade for 1-12 hours followed by slow cooling to room temperature (step **138**). The two electrode/ionomer devices should be then assembled by hot pressing in step **139**, where the ionomer/diluent layers should be in contact and the electrode layers should be on the outside. Appropriate ranges for the hot pressing parameters are 1-100 MPa, 100-200 degrees Centigrade, and 10 seconds-30 minutes.

[**0082**] Alternatively, the devices fabricated using the methods of **FIGS. 11 and 13** could be used in their water-swollen state. In this case, a water-miscible diluent should be used during the fabrication steps. Examples of appropriate water-miscible diluents include but are not limited to are glycerol, ethylene glycol, diethylene glycol, and triethylene glycol. The diluent should possess a high enough boiling point to be stable during the processing steps while also being water miscible. After the formation of the device by the methods described, the device should be boiled in deionized water in order to rinse the water miscible diluent out of the device and replace it with water. This boiling should be performed for 1-12 hours and the water may be replaced with fresh water several times during this processing. Additionally, the cation within the ionomer may be exchanged by soaking the device in an aqueous solution of a salt of the cation to be used.

EXAMPLES

Example 1

[**0083**] A Nafion-117 membrane was pretreated by boiling for one hour in 1.0 M sulfuric acid followed by boiling for one hour in deionized water. The membrane was then soaked in 0.5 M LiCl for 24 hours to exchange it into the lithium counterion form. The lithium exchanged membrane was then dried at 150 degrees Centigrade under vacuum for 12 hours. A section of this pretreated membrane was then soaked in neat 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ionic liquid at 150 degrees Centigrade for 4.5 hours. The uptake of ionic liquid was determined to be 45% of the dry weight of the membrane. Another section of the membrane was soaked in neat formamide at 60 degrees Centigrade for one hour. The uptake of formamide was 100% of the dry weight of the membrane.

[0084] An electrode mixture was prepared containing 36% (by weight) of a commercially available 5% Nafion suspension, 29% isopropyl alcohol, 29% deionized water, and 5% ruthenium (IV) oxide powder (diameter less than 1 micron, surface area 45-65 m^2/g). The mixture was stirred and sonicated for three hours to disperse the RuO_2 particles. This mixture was painted directly onto both sides of the diluent-swollen Nafion membranes. The volatile solvents were removed from the electrode mixture by placing the membranes under a heat lamp between painting each layer. A total of 20 layers were painted onto each side of the membranes. Following the painting process, the membranes were dried under vacuum at 130 degrees Centigrade for 10 minutes.

[0085] A mixture was then prepared containing 50% (by volume) of a commercially available 5% Nafion suspension and 50% isopropyl alcohol. A thin layer of this mixture was pained onto each side of the membranes. After drying of this layer, the membranes were positioned between two gold leafs on paper backing and loaded into a heated laminating press. For the ionic liquid-swollen membranes, the pressing was carried out at 180 degrees Centigrade under a pressure of 4 MPa for 15 seconds. For the formamide-swollen membranes, the pressing was carried out at 160 degrees Centigrade under a pressure of 4 MPa for 5 seconds.

[0086] The transducers thus formed are tested for their actuation performance. The actuators were clamped in a cantilevered configuration and a 2V step was applied. The displacement of the tip of the actuators was measured using a non-contact laser vibrometer and the strain at the outer surface of the actuators was computed from:

$$\varepsilon = \frac{\delta t}{L^2},$$

[0087] Where ϵ is strain, δ is the measured displacement, t is the thickness of the actuator, and L is the distance from the clamp to the point at which the displacement was measured. This equation assumes that the actuators bend with a constant curvature.

[0088] Both the ionic liquid- and formamide-swollen actuators generated approximately 1.2% strain in response to the 2V step input. The actuation speed was determined by taking the slope of the step response with respect to time for the first 2 seconds of the step. From this technique, the actuation speed was determined to be 0.04%/second for the ionic liquid-swollen actuator and 0.23%/second for the formamide-swollen actuator.

[0089] The 2V step was maintained for a period of 300 seconds during which the strain in the ionomeric actuators was measured. The strain had relaxed slightly in both actuators by the end of the test. The strain of the ionic liquid-swollen actuator decreased from a maximum of approximately 1.2% to approximately 1.1% after 300 seconds. The strain of the formamide-swollen actuator decreased from a maximum of approximately 1.2% to approximately 1.0% after 300 seconds.

Example 2

[0090] Four ionomer actuators were fabricated using the direct assembly process. Nafion-117 membranes were pretreated by boiling for one hour in 1.0 M H_2SO_4 followed by boiling for one hour in deionized water. The membranes were then soaked in 0.5 M LiCl for 24 hours to exchange it into the lithium counterion form. The lithium exchanged membranes were then dried at 150 degrees Centigrade under vacuum for 12 hours.

[0091] Sections of the pretreated membrane were soaked in ethylene glycol, diethylene glycol, triethylene glycol, and poly(ethylene glycol) (molecular weight **200**) at 60 degrees Centigrade for one hour. The diluent-swollen Nafion membranes were painted on both sides with an electrode mixture containing 36% (by weight) of a commercially available 5% Nafion suspension, 29% isopropyl alcohol, 29% deionized water, and 5% ruthenium (IV) oxide powder that had been stirred and sonicated for three hours to disperse the RuO_2 particles. The volatile solvents were removed from the electrode mixture by placing the membranes under a heat lamp between painting each layer; a total of 20 layers were painted onto each side of the membranes. Following the painting process, the membranes were dried under vacuum at 130 degrees Centigrade for 10 minutes.

[0092] A thin layer of a mixture containing 50% (by volume) of a commercially available 5% Nafion suspension and 50% isopropyl alcohol was then painted onto each side of the membranes. After drying of this layer, the membranes were positioned between two gold leafs on paper backing and loaded into a heated laminating press. The electrodes were bonded to the diluent-swollen membranes by pressing at 180 degrees Centigrade under a pressure of 4 MPa for 10 seconds.

[0093] The transducers thus formed were tested for their actuation performance. A 2V step was applied to the actuators in a cantilevered configuration. All four of the samples generated a strain of greater than 1.0% in response to the step voltage input. The largest strain of almost 2.0% was generated by the sample swollen with diethylene glycol. The actuation speed was also measured, by determining the slope of the step response with respect to time for the first two seconds after the step was applied. The actuation speed was found to be 0.07%/second for ethylene glycol, 0.13%/seconds for diethylene glycol, 0.12%/second for triethylene glycol, and 0.09%/second for poly(ethylene glycol).

Example 3

[0094] Nafion-117 membranes were pretreated by boiling for one hour in 1.0 M H_2SO_4 followed by boiling for one hour in deionized water. The membranes were then soaked in 0.5 M LiCl for 24 hours to exchange it into the lithium counterion form. The lithium exchanged membranes were then dried at 150 degrees Centigrade under vacuum for 12 hours. The membranes were swollen with triethylene glycol by soaking in neat triethylene glycol at 60 degrees Centigrade for one hour.

[0095] An electrode mixture was prepared containing 36% (by weight) of a commercially available 5% Nafion suspension, 29% isopropyl alcohol, 29% deionized water, and 5% ruthenium (IV) oxide powder (diameter less than 1 micron, surface area 45-65 m^2/g). The mixture was stirred and sonicated for three hours to disperse the RuO_2 particles. This mixture was painted directly onto both sides of the diluent-swollen Nafion membranes. The volatile solvents were removed from the electrode mixture by placing the membranes under a heat lamp between painting each layer. Four different samples were prepared and the thickness of the electrode was varied by varying the number of painted layers. The four samples had respectively, 12, 24, 36, and 48 layers painted on each side. Imaging by scanning electron

microscopy (SEM) indicated that for a membrane painted with 12 electrode layers, the electrode thickness was approximately 9.4 microns. Following the painting process, the membranes were dried under vacuum at 130 degrees Centigrade for 10 minutes.

[0096] A thin layer of a mixture containing 50% (by volume) of a commercially available 5% Nafion suspension and 50% isopropyl alcohol was then painted onto each side of the membranes. After drying of this layer, the membranes were positioned between two gold leafs on paper backing and loaded into a heated laminating press. The electrodes were bonded to the diluent-swollen membranes by pressing at 180 degrees Centigrade under a pressure of 4 MPa for 10 seconds.

[0097] The transducers thus formed were tested for their actuation performance. A 2V step was applied to the actuators in a cantilevered configuration. The maximum strain generated by the actuators was found to increase approximately linearly with increasing thickness of the electrode. The sample painted with 12 layers on each side generated a maximum strain of 0.54%, the sample with 24 layers generated a maximum strain of 0.82%, the sample with 36 layers generated a maximum strain of approximately 0.97%, and the sample with 48 layers generated a maximum strain of 1.14%. This indicates that the area of the ionomer/electrode interface is increased by increasing the thickness of the electrode, thus resulting in increased strain generation.

Example 4

[0098] Nafion-117 membranes were pretreated by boiling for one hour in 1.0 M H_2SO_4 followed by boiling for one hour in deionized water. The membranes were then soaked in 0.5 M LiCl for 24 hours to exchange it into the lithium counterion form. The lithium exchanged membranes were then dried at 150 degrees Centigrade under vacuum for 12 hours. The membranes were then swollen with ionic liquid by soaking in neat 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ionic liquid at 150 degrees Centigrade for 4.5 hours. The uptake of ionic liquid was 58% of the dry weight of the membranes.

[0099] Several electrode mixtures were prepared containing 47% (by weight) of a commercially available 5% Nafion suspension, 47% glycerol, and 6% metal powder. These mixtures were stirred and sonicated for three hours to disperse the metal particles. This will result in a mass loading of metal powder in the electrode that is 2.55 times greater than the mass of Nafion polymer in the electrode. The metal powder in the electrode layer was composed of a mixture of ruthenium (IV) oxide powder and gold flake. The composition of the mixture was varied from 100% ruthenium (IV) oxide to 100% gold with intermediate compositions of 25% gold, 75% RuO_2; 50% gold, 50% RuO_2; and 75% gold, 25% RuO_2. These compositions are expressed as a volumetric percentage of the electrode, where the ratio of 2.55 grams of metal to 1 gram of Nafion polymer in the electrode was held constant.

[0100] These mixtures were painted directly onto both sides of the ionic liquid-swollen Nafion membranes. The membranes were dried at 130 degrees Centigrade under vacuum for 15 minutes between each layer. This aggressive drying was necessary to remove the glycerol, which served to thicken the electrode mixture. A total of four layers were painted on each side of the membranes. After all of the layers were applied, the membranes were dried at 130 degrees Centigrade under vacuum for 10 minutes.

[0101] A thin layer of a mixture containing 50% (by volume) of a commercially available 5% Nafion suspension and 50% isopropyl alcohol was then pained onto each side of the membranes. After drying of this layer, the membranes were positioned between two gold leafs on paper backing and loaded into a heated laminating press. The electrodes were bonded to the diluent-swollen membranes by pressing at 210 degrees Centigrade under a pressure of 4 MPa for 30 seconds.

[0102] The transducers thus formed were tested for their actuation performance. A 2V step was applied to the actuators in a cantilevered configuration. The maximum strain generated by the actuators was found to increase with increasing content of ruthenium (IV) oxide. For the actuator with 100% RuO_2 electrode, the maximum strain generated in response to the 2V step was 0.4%. By contrast, the actuator with the 100% gold electrode generated less then 0.05% strain in response to the 2V step. However, the normalized actuation speed was found to increase by increasing the content of gold. The normalized actuation speed was obtained by dividing the initial slope of the step response (with respect to time) by the maximum strain achieved. From this method, the normalized actuation speed was found to be 1 s^{-1} for the actuator with the 100% RuO_2 electrodes, as compared to 6.7 s^{-1} for the actuator with the 100% gold electrodes. It can be seen that the electronic conductivity through the thickness of the electrode was increased by increasing the content of gold, which resulted in a faster actuation response. However, the area of the ionomer/conductor interface was increased by increasing the content of ruthenium (IV) oxide, which increased the maximum strain generated.

Example 5

[0103] A Nafion-117 membrane was pretreated by boiling for one hour in 1.0 M H_2SO_4 followed by boiling for one hour in deionized water. The membrane was then soaked in 0.5 M NaCl for 24 hours to exchange it into the sodium counterion form. The sodium exchanged membrane was then dried at 110 degrees Centigrade under vacuum for 12 hours.

[0104] An electrode mixture composed of 12.6% (by weight) of ruthenium (IV) oxide powder and 87.4% (by weight) of a commercially available 5% (by weight) Nafion dispersion was prepared. The mixture was stirred and sonicated for three hours to ensure dispersion of the RuO_2 particles. This mixture was then sprayed onto two fiberglass-reinforced Teflon decals in several coats using an airbrush. The pretreated and dried Nafion-117 membrane was positioned between these two decals and placed in a heated laminating press. The electrode layers were bonded to the Nafion membrane by pressing at 210 degrees Centigrade under a pressure of 14 MPa for 8 minutes.

[0105] After the pressing the assembly was allowed to cool to room temperature and the decals were peeled away. Following deposition of the electrodes, the membrane was treated by boiling for one hour in 1.0 M H_2SO_4 followed by boiling for one hour in deionized water. The electroded membrane was then cut into four strips and each strip was soaked in 0.5 M chloride salt solution for 72 hours to exchange it into a desired cation form. The four salt solutions used were lithium chloride, potassium chloride, cesium chloride, and tetraethylammonium chloride. After the ion exchange, the membranes were dried at 110 degrees Centigrade under vacuum for 12 hours. The dried membranes

were then soaked in a mixture of one part methanol to two parts 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ionic liquid for varying amounts of time in order to swell the membranes with a certain amount of ionic liquid. The membranes were then removed from the mixture and dried at 110 degrees Centigrade under vacuum to remove residual methanol.

[0106] Following the swelling of the devices with ionic liquid, a mixture was prepared containing 3% (by weight) of a poly(urethane urea) in a mixed solvent of 50% (by weight) isopropyl alcohol and 50% tetrahydrofuran. A thin layer of this mixture was painted onto each side of the membranes. After drying of this layer, the membranes were positioned between two gold leafs on paper backing and loaded into a heated laminating press. The gold leafs were bonded to the membranes by pressing at 180 degrees Centigrade under a pressure of 4 MPa for 10 seconds.

[0107] These transducers were tested for their actuation performance in a cantilevered free bender configuration. A 1.5V step was applied to the actuator and its displacement was measured using a non-contact laser vibormeter. By assuming that the actuator bent with constant curvature, the maximum strain generated was calculated. The actuation speed was determined by taking the slope of the step response for the first 20 milliseconds after the step was applied. By plotting the actuation speed versus the uptake of ionic liquid, it was clear that the actuation speed increased with increasing size of the cation exchanged into the membrane, for a given loading of ionic liquid. The size of the cations increases in the order lithium<potassium<cesium<tetraethylammonium. Representative results of this testing are shown in the following table.

cation	Uptake of ionic liquid (volume %)	Actuation speed (% strain per second)
lithium	31.8	0.069
potassium	24.9	0.380
cesium	30.5	0.331
tetraethylammonium	30.0	0.340

Example 6

[0108] Nafion-117 membranes were pretreated by boiling for one hour in 1.0 M H_2SO_4 followed by boiling for one hour in deionized water. The membranes were then soaked in 0.5 M LiCi for 24 hours to exchange it into the lithium counterion form. The lithium exchanged membranes were then dried at 150 degrees Centigrade under vacuum for 12 hours. The membranes were then swollen with ionic liquid by soaking in neat 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ionic liquid at 150 degrees Centigrade for 4.5 hours.

[0109] Several electrode mixtures were prepared containing a commercially available 5% suspension of Nafion, isopropyl alcohol, and conducting powder. The conducting powders used were ruthenium (IV) oxide, single walled carbon nanotubes (SWNT), and polyaniline. For ruthenium (IV) oxide, 8 mixtures were prepared containing between 12% and 67% RuO_2, where the RuO_2 content is expressed as a percentage of the electrode volume (RuO_2+Nafion, without the volatile components). For single walled carbon nanotubes, 5 mixtures were prepared, containing between 5% and 40% (by volume) of SWNT. For polyaniline, 4 mixtures were prepared, containing between 50% and 100% polyaniline.

[0110] These mixtures were painted directly onto both sides of ionic liquid-swollen Nafion membranes and dried. A mixture of 50% isopropyl alcohol and 50% of a commercially available 5% Nafion dispersion was painted over this layer and dried. The membranes were placed between two paper-backed gold leafs and hot pressed at 4 MPa and 180 degrees Centigrade for 15 seconds.

[0111] The membranes thus fabricated were tested for their actuation performance. The actuators were clamped in a cantilevered configuration and a 2V step input was applied. The displacement of the free end was measured and the strain generated by the actuators was computed by assuming that they bent with a constant curvature. The actuation speed was determined by taking the slope of the step response for the first two seconds after the step was applied.

[0112] The actuation speed of the transducers is controlled by the rate with which the charge double layer can form at the ionomer/conductor interface. The rate at which the double layer can form is limited by two factors: diffusion of electrons within the electronically conductive phase and diffusion of ions within the ionically conductive phase. Based on this understanding, it is expected that a tradeoff will exist between increasing the content of ionomer and increasing the content of electronically conducting particles.

[0113] For the RuO_2 electroded actuators, the actuation speed was observed to increase with increasing content of RuO_2 powder until a loading of 45% (by volume), at which point the actuation speed was observed to decrease. Below a loading of 45%, the actuation speed was limited by the speed of electron diffusion within the electronically conductive phase because of the low content of this phase. Above 45%, the actuation speed was limited by the diffusion of ions within the ionomer phase because of the low content of ionomer. At a loading of RuO_2 powder of 45%, the limiting effect of these factors was balanced and the maximum actuation speed was observed.

[0114] Similar experiments were performed for the actuators with SWNT electrodes and polyaniline electrodes. For the membranes electroded with SWNT, the actuation speed was observed to increase with increasing content of SWNT until a loading of 30%. Above this loading, the actuation speed was observed to decrease. The lower optimal loading of SWNT as compared to RuO_2 can be explained by considering that the electronic conductivity of SWNT is higher than RuO_2. Also, the carbon nanotubes have a high aspect ratio and therefore form a percolative conductive network at a lower volumetric loading than the roughly spherical RuO_2 particles. Therefore, less content of SWNT is required to achieve the same electronic conductivity in the electrode. By contrast, the highest actuation speed for the actuators with the polyaniline electrodes was observed to occur at a loading of 95% of polyaniline by volume. This can be explained by considering that the polyaniline particles that were used possess a low electronic conductivity and are also ionically conductive.

Example 7

[0115] A Nafion-117 membrane was pretreated by boiling for one hour in 1.0 M H_2SO_4 followed by boiling for one hour in deionized water. The membrane was then soaked in 0.5 M LiCl for 24 hours to exchange it into the lithium

counterion form. The lithium exchanged membrane was then dried at 150 degrees Centigrade under vacuum for 12 hours. The membrane was then swollen with formamide by soaking in neat formamide at 60 degrees Centigrade for one hour.

[0116] An electrode mixture was prepared containing a commercially available 5% Nafion dispersion, isopropyl alcohol, ruthenium (IV) oxide powder, and single walled carbon nanotubes (SWNT). The mixture was composed such that the resulting electrode would contain 10% (by volume) of SWNT and 35% (by volume) of RuO_2. The electrode mixture was stirred and sonicated for five hours in order to disperse the RuO_2 and SWNT particles. The electrode mixture was painted directly onto both sides of the formamide-swollen Nafion membrane in many layers, with drying under a heat lamp between each layer. The Nafion membrane was taped to an aluminum plate during the painting process. This plate was fitted with a piezoceramic wafer that was excited with a 40 kHz signal throughout the electrode formation step. This high frequency vibration of the membrane ensured that the carbon nanotubes did not coagulate prior to formation of the electrode layers. The electrode mixture was stirred and sonicated between the painting of each layer.

[0117] A mixture of 50% isopropyl alcohol and 50% of a commercially available 5% Nafion dispersion was then painted over this layer and dried. The membranes were placed between two paper-backed gold leafs and hot pressed at 4 MPa and 160 degrees Centigrade for 5 seconds.

[0118] The actuator thus fabricated was tested for its actuation performance. The actuator was clamped in a cantilevered configuration and a 2V step was applied across its thickness. The displacement of the free end was measured with a laser vibrometer and the strain generated by the actuator was computed by assuming that it bent with constant curvature. The maximum strain measured was 4.7%. The actuation speed was determined by taking the slope of the step response for the first 2 seconds after the step was applied. The measured actuation speed of the transducer was 1%.

Example 8

[0119] A Nafion-117 membrane was pretreated by boiling for one hour in 1.0 M H_2SO_4 followed by boiling for one hour in deionized water. The membrane was then soaked in 0.5 M LiCl for 24 hours to exchange it into the lithium counterion form. The lithium exchanged membrane was then dried at 150 degrees Centigrade under vacuum for 12 hours. The membrane was then swollen with ionic liquid by soaking in neat 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ionic liquid at 150 degrees Centigrade for 4.5 hours.

[0120] An electrode mixture was prepared containing 47% (by weight) of a commercially available 5% Nafion suspension, 47% glycerol, and 6% ruthenium (IV) oxide powder. This mixture was stirred and sonicated for three hours to disperse the metal particles. The electrode mixture was painted directly onto both sides of the ionic liquid-swollen Nafion membrane. The membrane was dried at 130 degrees Centigrade under vacuum for 15 minutes between each layer. This aggressive drying was necessary to remove the glycerol, which served to thicken the electrode mixture. A total of four layers were painted on each side of the membrane. After all of the layers were applied, the membranes were dried at 130 degrees Centigrade under vacuum for 10 minutes.

[0121] A thin layer of a mixture containing 50% (by volume) of a commercially available 5% Nafion suspension and 50% isopropyl alcohol was then pained onto each side of the membrane. After drying of this layer, the membrane was positioned between two gold leafs on paper backing and loaded into a heated laminating press. The electrodes were bonded to the ionic liquid-swollen membrane by pressing at 210 degrees Centigrade under a pressure of 4 MPa for 30 seconds.

[0122] The transducer thus fabricated was tested for its actuation performance. The actuator was clamped in a cantilevered configuration in air and a 2V, 1 Hz sine wave input was applied. The displacement of the free end was measured using a laser vibrometer and the strain generated by the actuator was computed by assuming that it bent with constant curvature. After 100 actuation cycles, the strain generated by the actuator was measured to be 0.1%. After cycling the actuator continuously for over 250,000 cycles, the strain generated was measured to be 0.1%. Also, the strain generated exhibited very little variation over the course of the testing. This experiment demonstrates that the transducers of this invention can be operated for long periods of time in air with little or no loss of performance.

Example 9

[0123] A membrane composed of sulfonated poly(arylene thioether sulfone) (PATS) with a degree of sulfonation of 30% was pretreated by boiling for one hour in 1.0 M H_2SO_4 followed by boiling for one hour in deionized water. The membrane was then soaked in 0.5 M NaCl for 24 hours to exchange it into the sodium counterion form. The sodium exchanged membrane was then dried at 150 degrees Centigrade under vacuum for 12 hours.

[0124] An electrode mixture was prepared containing 47% (by weight) of a commercially available 5% Nafion suspension, 47% glycerol, and 6% ruthenium (IV) oxide powder. This mixture was stirred and sonicated for two hours to disperse the particles. Electrodes were formed from this mixture by painting onto two fiberglass-reinforced Teflon decals. Each layer was dried at 130 degrees Centigrade under vacuum for 15 minutes prior to painting of the next layer. A total of six layers were painted. The decals were then positioned on each side of the dry PATS membrane and hot pressed to the membrane at 210 degrees Centigrade and 20.6 MPa for 8 minutes.

[0125] After cooling to room temperature, the decals were peeled away and the electroded membrane was boiled in 1.0 M sulfuric acid followed by boiling in deionized water. The membrane was then soaked in an aqueous solution of 0.01 M tetraammineplatinum chloride overnight. The membrane was rinsed and the absorbed tetraammineplatinum ions were reduced by soaking in 0.05% (by weight) aqueous sodium borohydride solution for 5 hours. The membrane was then boiled in 1.0 M sulfuric acid. The platinum surface layers that were formed were then coated with gold by electroplating using a commercially-available gold electroplating solution.

[0126] The membrane was then boiled in 1.0 M sulfuric acid for one hour followed by rinsing with deionized water and boiling in 1.0 M lithium chloride solution for two hours. This last step exchanged the membrane to the lithium counterion form.

[0127] The actuator thus fabricated was tested for its actuation performance. The actuator was clamped in a

cantilevered configuration and a random voltage input was applied across its thickness. The displacement of the free end was measured with a laser vibrometer and the strain generated by the actuator was computed by assuming that it bent with constant curvature. A Fourier analyzer was used to calculate the transfer function between the free strain and the applied voltage. At low frequency (less than 1 Hz), the magnitude of this transfer function was found to be 0.15%/V.

[0128] Those of skill in the art will recognize that the invention can be practiced with modification within the scope and spirit of the appended claims.

What is claimed is:

1. An ionomeric device having an electrode structure, comprising:

an ionomer membrane;

one or more layers of a composition comprising an ionomeric polymer and electronically conducting particles hot pressed on one or more surfaces of said ionomer membrane;

a diluent within said ionomer membrane and said one or more layers of said composition; and

one or more layers of an electronically conducting material on each of said one or more layers of said composition.

2. An ionomeric device having an electrode structure, comprising:

an ionomer membrane;

one or more layers of a composition comprising an ionomeric polymer and electronically conducting particles positioned on one or more surfaces of said ionomer membrane;

one or more nanowires which extend through said one or more layers of said composition;

a diluent within said ionomer membrane and said one or more layers of said composition; and

one or more layers of an electronically conducting material on each of said one or more layers of said composition.

3. The ionomeric device of claim 1 configured as a sensor.

4. The ionomeric device of claims **1** configured as a transducer.

5. The ionomeric device of claims **1** configured as an actuator.

6. The ionomeric device of claim 1 wherein said ionomeric polymer of said composition and said ionomer membrane includes a counterion selected from the group consisting of alkylammonium ions, alkali metal ions, or alkaline earth metal ions.

7. The ionomeric device of claim 2 wherein said ionomeric polymer of said composition and said ionomer membrane includes a counterion selected from the group consisting of alkylammonium ions, alkali metal ions, or alkaline earth metal ions.

8. The ionomeric device of claim 1 wherein said ionomer membrane is selected from the group consisting of perfluorosulfonated polymers, perfluorocarboxylated polymers, sulfonated poly(arylene ether sulfone), sulfonated poly(arylene thioether sulfone), sulfonated poly(ether ketone ketone), sulfonated polystyrene, and sulfonated butadiene.

9. The ionomeric device of claim 8 wherein said ionomer membrane is Nafion.

10. The ionomeric device of claim 2 wherein said ionomer membrane is selected from the group consisting of perfluorosulfonated polymers, perfluorocarboxylated polymers, sulfonated poly(arylene ether sulfone), sulfonated poly(arylene thioether sulfone), sulfonated poly(ether ketone ketone), sulfonated polystyrene, and sulfonated butadiene.

11. The ionomeric device of claim 10 wherein said ionomer membrane is Nafion.

12. The ionomeric device of claim 1 wherein said diluent is selected from the group consisting of water, formamide, ethylene glycol, diethylene glycol, triethylene glucol, poly-(ethylene glycol), and ionic liquids.

13. The ionomeric device of claim 12 wherein said ionic liquid is 1-ethyl-3-methylimidazolium trifluoromethanesulfonate.

14. The ionomeric device of claim 1 wherein said diluent is selected from the group consisting of water, formamide, ethylene glycol, diethylene glycol, triethylene glucol, poly-(ethylene glycol), and ionic liquids.

15. The ionomeric device of claim 14 wherein said ionic liquid is 1-ethyl-3-methylimidazolium trifluoromethanesulfonate.

16. The ionomeric device of claim 1 wherein said electronically conducting particles are comprised of a material selected from the group consisting of metals, metal oxides, and conducting polymers.

17. The ionomeric device of claim 1 wherein said electronically conducting particles are comprised of a material selected from the group consisting of ruthenium (IV) oxide, polypyrrole, polyaniline, carbon, carbon nanotubes, and gold.

18. The ionomeric device of claim 2 wherein said electronically conducting particles are comprised of a material selected from the group consisting of metals, metal oxides, and conducting polymers.

19. The ionomeric device of claim 2 wherein said electronically conducting particles are comprised of a material selected from the group consisting of ruthenium (IV) oxide, polypyrrole, polyaniline, carbon, carbon nanotubes, and gold.

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