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(54) **NOVEL ELECTRICALLY ACTIVE IONIC POLYMER METAL COMPOSITES AND NOVEL METHODS OF MANUFACTURING THEM**

(75) Inventors: **Mohsen Shahinpoor**, Albuquerque, NM (US); **Massoud Ahghar**, Albuquerque, NM (US); **Niculina Cristina Popa**, Albuquerque, NM (US)

Correspondence Address:
MOHSEN SHAHINPOOR
909 VIRGINIA, NE, SUITE 205
ALBERQUERQUE, NM 87108 (US)

(73) Assignees: **Dr. Mohsen Shahinpoor**; **Environmental Robots Inc.**, Albuquerque, NM (US)

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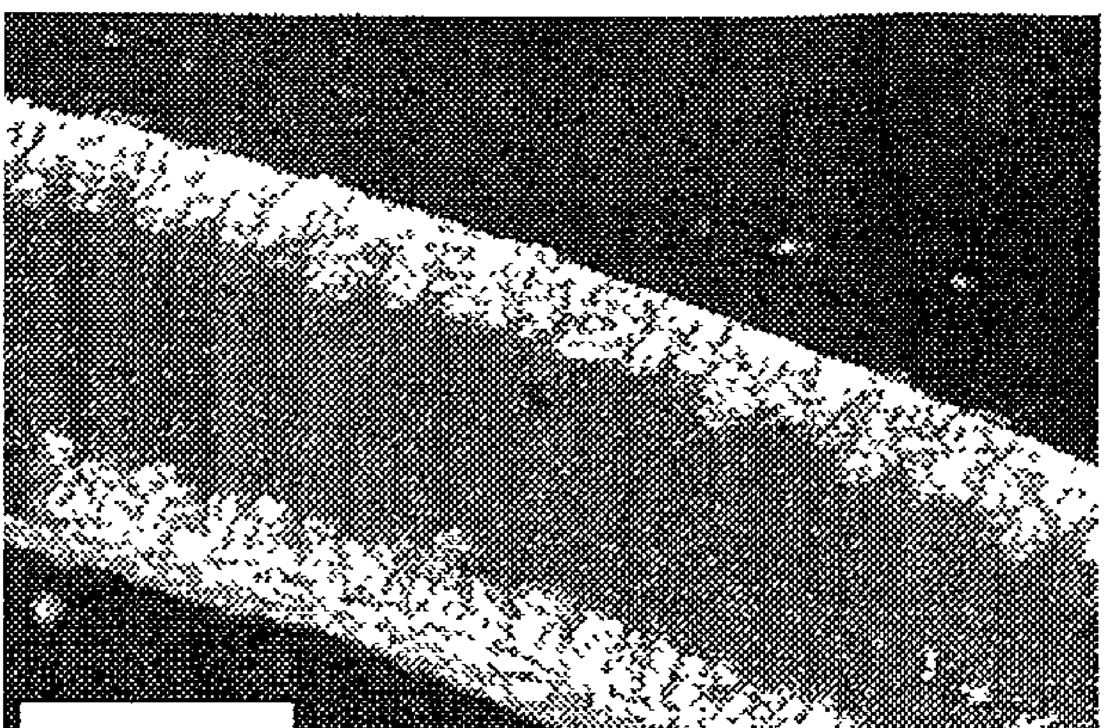
(57) **ABSTRACT**

Novel electrically active ionic polymer metal composite materials and novel methods of manufacturing them by means of a series of innovative chemical processes of first chemically depositing none noble metal salt cations inside a cationic polymer molecular network followed by chemical reduction of the said none noble metal salt cations to generate reduced none noble metal particles deposited inside the polymeric molecular network followed by a second electro or chemo deposition and plating of a noble metal inside and on the surfaces of the reduced none noble metallic particles in the said polymer molecular network to protect the first said none noble metal particles from oxidation, corrosion and chemical degradation for prolonged sensing and actuation applications of the said novel ionic polymer metal composite material which generates an electrical signal with mechanical deformation and undergoes mechanical deformation if an electric field is imposed on it.



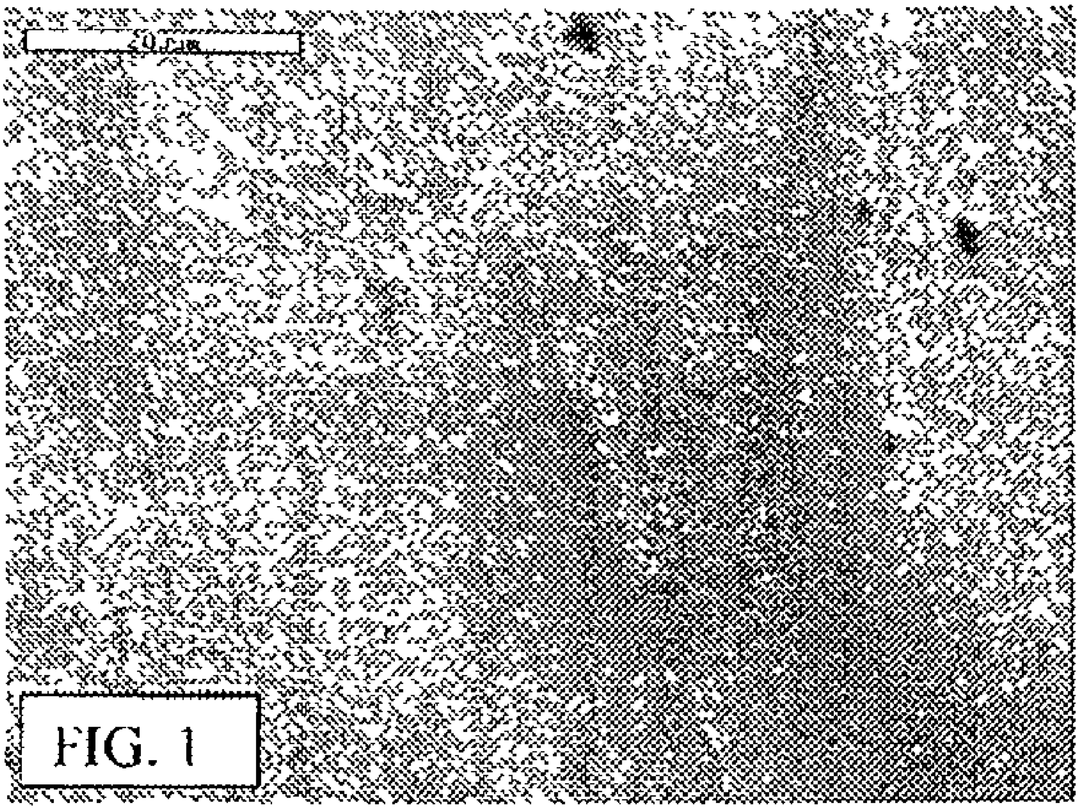


FIG. 1

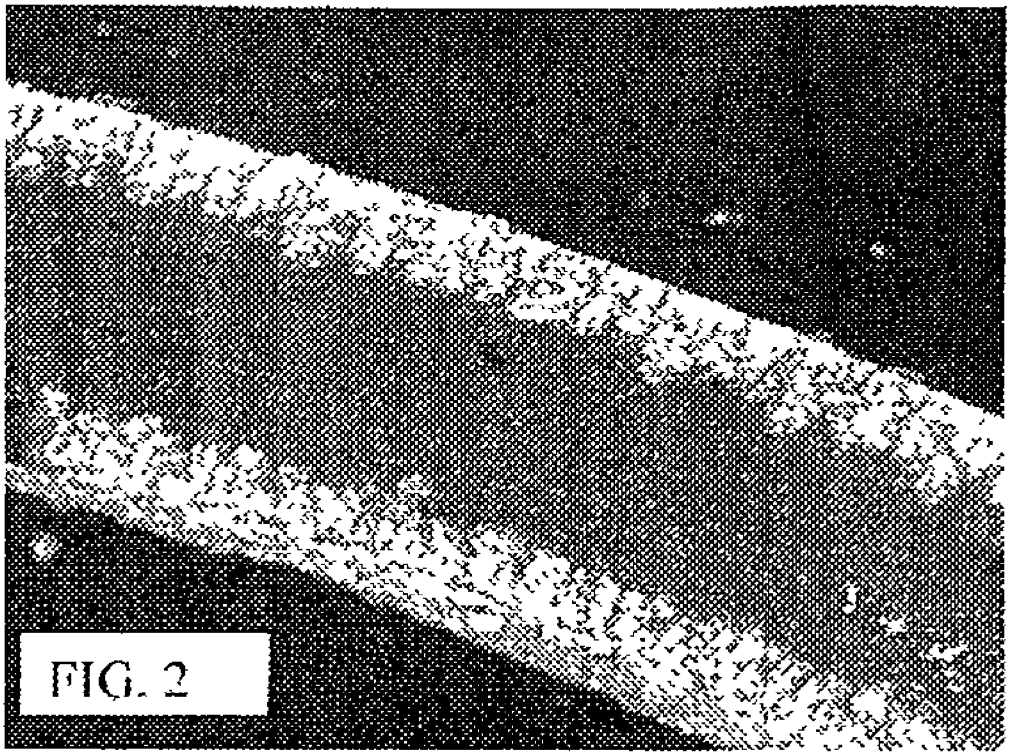


FIG. 2

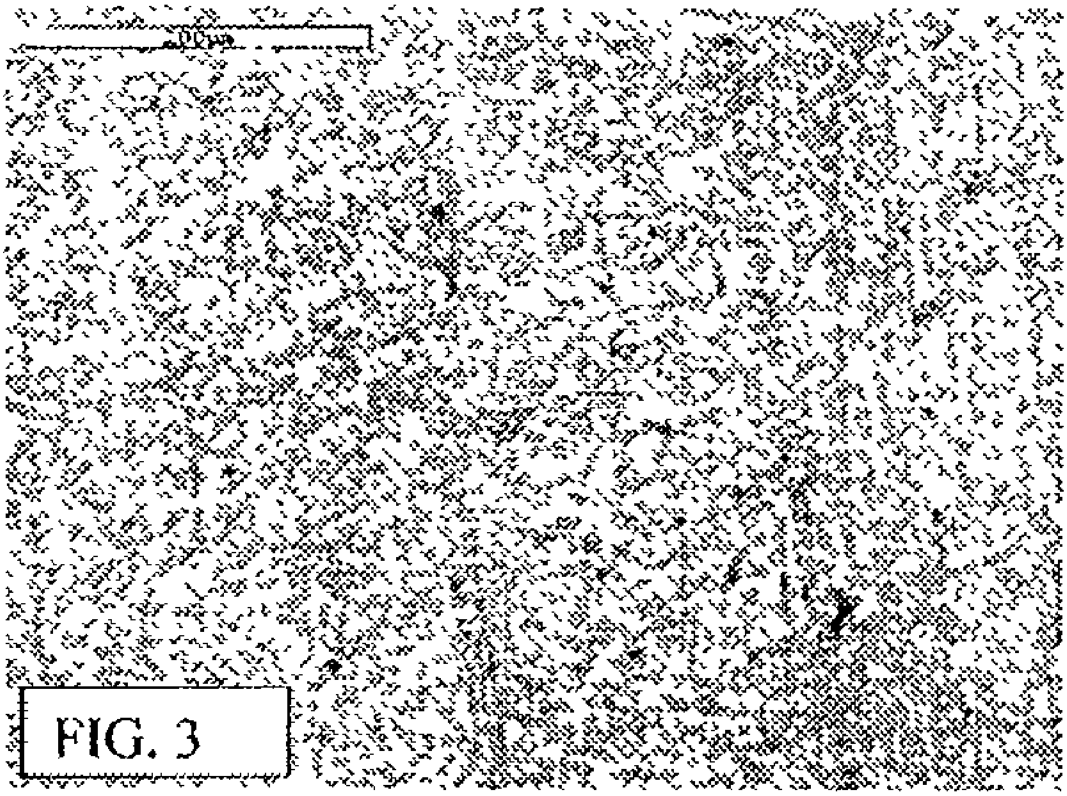


FIG. 3

NOVEL ELECTRICALLY ACTIVE IONIC POLYMER METAL COMPOSITES AND NOVEL METHODS OF MANUFACTURING THEM

BACKGROUND OF INVENTION

[0001] The present invention relates to novel electrically active ionic polymer metal composite materials and novel methods of manufacturing them.

[0002] The creation of ionic polymer metal composite materials made from polymers and polyelectrolytes are relatively new but also fairly well known.

[0003] U.S. Pat. No. 6,403,245, to Hunt, discloses that a electro-catalyst is typically provided as a thin layer adjacent to the ion-exchange membrane (see also U.S. Pat. Nos. 5,132,193 and 5,409,785). The electro-catalyst layer is typically applied as a coating to one major surface of a sheet of porous, electrically conductive sheet material or to one surface of the ion-exchange membrane. The Phosphoric Acid Fuel Cells (PAFCs), which are the most commercially developed fuel cells, typically use 90 ozs. of platinum in a 500 kw unit, with 80-85% of the metal being recoverable by recycling. With the development of PAFCs, the power industry is poised to provide a source of fuel that is clean, efficient, noiseless and abundant. For the applications, other types of fuel cells, such as Proton Exchange Membrane Fuel Cells (PEMFCs), pose a better solution. PEMFCs offer a technology that has an acceptable power to weight ratio, and which is also clean, efficient and noiseless. The electro-catalyst layers compromising platinum and platinum-group elements, both for anode and cathode, are presently a high-cost component of PEMFCs. Studies have shown that the catalyst accounts for $2-3 of the total cost of $15-21/kilowatt. Most of the fuel cell cost is related to the membrane area via current collectors, seals, etc. Accordingly, there is a desire to achieve cost reduction through higher catalyst efficiency by increasing the power per unit area. Although PAFC technology is well suited for use in power plant fuel cell facilities, their high weight-to-power ratio makes PAFC technology a poor fit for use in vehicles, such as zero-emission vehicles (ZEVs), presently needed to reduce pollution in densely populated areas.

[0004] U.S. Pat. No. 6,109,852, to Shahinpoor et al., discloses a chemical coating and reduction, mechanical/electrical treatment of ion-exchange materials to convert them to synthetic muscles. The actuator of the invention showing the treated membrane actuator with electrodes placed at one end of the membrane, the electrodes being further attached to a power source. Synthetic muscles created by the proposed method are capable of undergoing electrically controllable large deformations resembling the behavior of biological muscles. Plus, a metal salt deposit on membrane used a noble metal palladium, nickel or platinum.

[0005] U.S. Pat. No. 5,389,222, to Shahinpoor discloses electrically controllable polymeric gel actuators or synthetic muscles, using gels made of polyvinyl alcohol, polyacrylic acid, polyacrylonitrile, or polyacrylamide contained in an electrolytic solvent bath. These actuators operate by reacting to changes in the ionization of a surrounding electrolyte by expanding or contracting, and can be spring-loaded and/or mechanically biased for specific applications. Polymeric gel configurations such as sheets, solid shapes or fiber aggregates are contemplated, as are the use of a salt water solution for the electrolyte, and a platinum catalyst in the actuator housing to recombine the hydrogen and oxygen produced as a result of electrolysis during ionization of the electrolyte. Again, liquid containment is required to maintain strength and electric controllability, and not enough deformation or displacement is generated.

[0006] U.S. Pat. No. 5,268,082, to Oguro et al., discloses an actuator element based comprises an ion exchange membrane and a pair of electrodes attached to opposite surfaces of the ion exchange membrane; the ion exchange membrane in a water-containing state being caused to bend and/or deform by application of an electric potential difference thereacross.

[0007] U.S. Pat. No. 5,250,167, to Adolf, et al., discloses actuators or synthetic muscles, using polymeric gels contained in compliant containers with their solvents; these actuators undergo substantial expansion and contraction when subjected to changing environments. The actuators may be rigid or flexible and may be computer-controlled. The driver may also be electrolytic, where application of a voltage across the polymer gel causes a pH gradient to evolve between the electrodes. For example, filling the polymer fibers with platinum by alternatively treating them with solutions of platinic chloride and sodium borohydride obtains a reversible expansion and contraction of the fiber with the application of an electric field. The actuating gel itself is the only moving part required and the electric field may be only on the order of a few volts per centimeter. The disadvantage is that actuator performance is dictated by the parameters of the polymeric gel used. Furthermore, liquid containment is required to make the actuators stronger and not so easily broken.

[0008] U.S. Pat. No. 5,100,933, to Tanaka, et al., discloses the use of ionized crosslinked polyacrylamide gels as engines or synthetic muscles; the gels can contain a metal ion and are capable of discontinuous volume changes induced by infinitesimal changes in environment. The gel is made by dissolving acrylamide monomers and bisacrylamide monomers in water, adding a polymerization initiator (in particular, ammonium persulfate and TEMED, or tetramethyl-ethylene-diamin-e) to the solution, soaking the gel sample in water to wash away all residual monomers and initiators, immersing the gel in a basic solution of TEMED for up to 60 days, then immersing the gel in a solvent (in particular, acetone, acetone in water, ethanol and water, or methanol and water). The primary disadvantages of these actuators are generally that the response time of the gel is much longer than that of other known actuator components and that the gel must be contained in the solvent bath. The gels are also mechanically brittle and easily broken.

[0009] U.S. Pat. No. 4,522,698, to Maget, discloses a prime mover that uses pressure increases and decreases induced by converting molecules of electrochemically active material to ions, transporting ions through an electrolytic membrane and reconverting the ions to molecules. The prime mover includes gas-tight compartments filled with an electrochemically active material and separated by an electrolytic membrane, such as an ion-exchange membrane, that incorporates electrodes so that a voltage gradient can be established across the membrane to induce current flow through the membrane. When the current flows through the membrane, molecules travel through the membrane and are reconverted to molecules in the opposite compartment causing a pressure increase in the receiving compartment and a pressure decrease in the other compartment. The pressure changes are converted to mechanical motion that can be used as a driver for a mechanical load. The disadvantages of this technique are that the resulting motion is small and the pressure increase may rupture the membrane.

[0010] U.S. Pat. No. 4,364,803, to Nidola et al., discloses a process for deposition of catalytic electrodes on ion-exchange membranes and an electrolytic cell made by the process. The process involves contacting a water-swollen, roughened membrane with an amphoteric organic or metal salt thereof, such as alkali metal salts thereof, e.g., platinum, palladium, and nickel. After further processing, the membrane is then contacted with a solution of the selected metal salt wherein sorption of the metal salts takes place mainly on the membrane surface in the vicinity of the polar groups of the polymer or the pre-adsorbed polar groups of the amphoteric organic. The absorbed/adsorbed metal creates the catalytic electrodes. The patent discloses operation of the electrode in the presence of sodium brine/caustic soda.

[0011] "Development of a Novel Electrochemically Active Membrane and Smart Material Based Vibration Sensor/Damper," by Sadeghipour et al., Smart Materials and Structures, Vol. 1, pp. 172-179, (1992), discloses "smart" materials developed from metalized NAFION membranes that may be used for vibration sensing and damping applications. For sensing applications, the smart NAFION based viscoelastic material generates a voltage response when subject to mechanical vibrations. For damping applications, the material dissipates mechanical or pressure induced voltage potentials (electrical energy) as heat energy. The article also discloses a method of making the smart materials comprising steps of platinum deposition onto a NAFION, membrane and saturation of the platinum coated metal with hydrogen under high pressure, or alternatively, exposing the platinum coated membrane to dissolved hydrogen. Applications for the smart material include integration into cantilever structures, such as robot arms, aircraft wings, etc., for damping; use as a vibration cell accelerometer; and use as a pressure cell. For vibration cell sensors, the authors reported voltage response over the frequency range of approximately 100 Hz to approximately 3000 Hz. Load response was also reported at 500 Hz and 1000 Hz. A plot of simulated tip deflection versus time for an electrically damped metal-NAFION composite beam were reported for initial positive tip deflections of 1% of beam length. Because no beam lengths were given, the magnitude of displacement cannot be determined.

[0012] Therefore, the above review of the pertinent literature clearly indicates that current electrically active ionic polymer metal composite materials manufacturing processes and materials cost are expensive due to exclusive use of noble metal salts such as platinum, palladium and gold as penetrating metal particles. Further, such noble metals do no provide highly conductive metal particles, which are desirable, such as silver and copper, into the ionic network. Thus, there is an existing need for novel materials and methods of manufacturing electrically active ionic polymer metal composite materials to be cost effective and economical for mass production. Thus, in this disclosure we introduce a unique electro or chemo deposition and chemical plating methodology to chemically deposit highly conductive none noble metal particles in the ionic polymeric network first and then electrically or chemically plate the none noble metal particles with noble metals. In this manner we embed in the ionic polymer first a highly electrically conductive phase of none noble metal particles first, which is highly desirable for sensing and actuation properties of these electrically active ionic polymer metal composites or IPMC"s and then we electroplate or chemo plate the none noble metal particles with a noble metal such as Gold or platinum.

SUMMARY OF INVENTION

[0013] This invention describes novel electrically active ionic polymer metal composite materials and novel methods of manufacturing them by means of a series of innovative chemical processes of first chemically depositing none noble metal salt cations inside a cationic polymer molecular network followed by chemical reduction of the said none noble metal salt cations to generate reduced none noble metal particles deposited inside the polymeric molecular network followed by a second electro or chemo deposition and plating of a noble metal inside and on the surfaces of the reduced none noble metallic particles in the said polymer molecular network to protect the first said none noble metal particles from oxidation, corrosion and chemical degradation for prolonged sensing and actuation applications of the said novel ionic polymer metal composite material which generates an electrical signal with mechanical deformation and undergoes mechanical deformation if an electric field is imposed on it.

BRIEF DESCRIPTION OF DRAWINGS

[0014] The accompanying Figures, which are incorporated into and form a part of the specification, illustrate several embodiments of the present invention and, together with the description, serve to explain the principles of the invention. However, these Figures, as well as the following detailed description and the examples are only for the purpose of illustrating a preferred embodiment of the invention and are not to be construed as limiting the invention. In the drawings:

[0015] **FIG. 1** is a perspective view of a none noble metal ionic polymer molecular network with surface Gold.

[0016] **FIG. 2** is a perspective view of the ionic polymer molecular network with none noble metal deposition showing the dendritic penetration of said none noble metal into ionic polymer molecular network as well as the Gold surface plating on top.

[0017] **FIG. 3** is a perspective view of the none noble metal ionic polymer composite with its Gold plated roughened surface.

DETAILED DESCRIPTION

[0018] This invention describes first novel ionic polymer metal composites manufactured by means of an innovative chemical depositing process, the process comprising the steps of: first depositing none noble metal salt cations inside a cationic polymer molecular network followed by chemical reduction of the said none noble metal salt cations to generate reduced none noble metal particles deposited inside the polymeric molecular network and the outside surfaces of the polymeric material, like outside metallic electrodes, followed by a second electro or chemo deposition and plating of a noble metal inside and on surfaces of the said reduced none noble metal particles in the said polymer molecular network to protect the first said none noble metal particles from oxidation, corrosion and chemical degradation for prolonged sensing and actuation applications of the said novel ionic polymer metal composite material which generates an electrical signal with mechanical deformation and undergoes mechanical deformation if an electric field is imposed on it.

[0019] The invention further describes the manufacturing processes for the novel ionic polymer metal composite materials, further comprising the steps of: adding dispersing chemicals to the said chemical reduction process, wherein said addition of a dispersing agent prevents reduced noble and none noble metal particles to coalesce and helps forming uniformly distributed none noble metal particles chemically deposited inside the ionic polymer network and further helps them to penetrate deeper into the said ionic polymer molecular network.

[0020] The invention further describes the manufacturing processes for the novel ionic polymer metal composite materials, further comprising the steps of: adding an alcohol solvent to the reduction solution, wherein said addition of an alcohol solvent such as isopropyl and ethyl alcohol, help expand the ionic polymer network and enhances deeper penetration of none noble and noble metal particles into said ionic polymer molecular network.

[0021] The invention further describes the manufacturing processes for the novel ionic polymer metal composite materials, further comprising the steps of: mechanically stretching the said ionic polymer before the start of manufacturing processes, wherein said mechanical stretching helps expand the ionic polymer network and enhances deeper penetration of none noble and noble metal particles into said ionic polymer molecular network.

[0022] The invention further describes yet a family of novel ionic polymer metal composites to be used as electromechanical sensors in the sense that if they are mechanically moved or deformed they generate an electrical voltage across their surface electrodes. Typical values are that for a cantilever sample of such active materials of dimensions 20 mm×5 mm×0.2 mm flipped atone end by 10 mm, generates up to 10 mV across its surface electrodes.

[0023] The invention further describes yet another family of novel ionic polymer metal composites to be used as electromechanical actuators, transducers and artificial muscles in the sense that if they are electrically activated by placing an electric field across their surface electrodes of a cantilever sample in a bending actuator configuration, they move or bend or flip dynamically like a wing with time varying electric fields. Typical values are that a cantilever sample of such active materials of dimensions 20 mm×5 mm×0.2 mm placed in an electric field of 5 mV/μm generates a bending deflection of about 10 mm at its free end.

[0024] The invention finally describes means of encapsulating the novel ionic polymer metal composite materials inside a flexible polymeric membrane to keep it hermetically sealed and moist and to provide additional outside protection.

[0025] None noble metal manufacturing of ionic polymers results in sensors, actuators, and synthetic muscles with enhanced overall sensitivity and actuation response compared with noble metal manufacturing.

[0026] In another preferred embodiment of the present invention, dispersing agents are used create a more uniform distribution of reduced metallic particles both for none noble and noble metal particles deposited inside on the molecular network and on the surfaces of the ionic polymer.; Some of the dispersing agents used are polyvinylpyrrolidone; poly(1-vinylpyrrolidone-co-vinyl acetate); poly(1-vinylpyrrolidone-co-2-dimethylamino ethyl methacrylate).

[0027] Several preferred embodiments of the present invention can be encapsulated with an impermeable flexible outer membrane to keep the ionic polymer metal composite moist and prevent it from drying up.

[0028] The novel material and the novel methods of manufacturing them in this invention also have applications in such as making membrane electrode assemblies (fuel cells), ionic exchange membrane metal deposit, sensors, actuators, transducers and synthetic muscles. The limitations associated with existing ionic polymer metal composites materials and the methods for their manufacture are overcome by the present invention which provides novel methods of manufacturing and novel materials that are electrically active ionic polymer metal composites.

[0029] Although the present invention has been described in terms of the presently preferred embodiments, it is to be understood that the disclosure is not to be interpreted as limiting. Various alterations and modifications will no doubt become apparent to those skilled in the art after having read the above disclosure. Accordingly, it is intended that the appended claims be interpreted as covering all alterations and modifications as fall within the true spirit and scope of the invention.

1. Novel ionic polymer metal composites manufactured by means of an innovative chemical depositing process, the process comprising the steps of: first depositing none noble metal salt cations inside a cationic ionic polymer molecular network followed by chemical reduction of the said none noble metal salt cations to generate reduced none noble metal particles deposited inside the polymeric molecular network and the outside surfaces of the polymeric material, like outside metallic electrodes, followed by a second electro or chemo deposition and plating of a noble metal inside and on surfaces of the said reduced none noble metal particles in the said polymer molecular network to protect the first said none noble metal particles from oxidation, corrosion and chemical degradation for prolonged sensing and actuation applications of the said novel ionic polymer metal composite material which generates an electrical signal with mechanical deformation and undergoes mechanical deformation if an electric field is imposed on it.

2. The manufacturing processes for the novel ionic polymer metal composite material of claim 1, further comprising the steps of: first depositing none noble metal salt cations inside a cationic polymer molecular network and the outside surfaces of the polymeric material, like outside metallic electrodes, followed by chemical reduction of the said none noble metal salt cations to generate reduced none noble metal particles deposited inside the polymeric network, followed by a second electro or chemo deposition and plating of a noble metal inside and on surface of the said reduced none noble metal particles in the said polymer molecular network to protect the first said none noble metal particles from oxidation, corrosion and chemical degradation for prolonged sensing and actuation applications of the said novel ionic polymer metal composite material which generates an electrical signal with mechanical deformation and undergoes mechanical deformation if an electric field is imposed on it.

3. The manufacturing processes for the novel ionic polymer metal composite material of claim 1, as described in claims **1** and **2** further comprising the steps of: adding dispersing chemicals to the said chemical reduction process, wherein said addition of a dispersing agent prevents reduced noble and none noble metal particles to coalesce and helps forming uniformly distributed none noble metal particles chemically deposited inside the ionic polymer network and further helps them to penetrate deeper into the said ionic polymer molecular network.

4. The manufacturing processes for the novel ionic polymer metal composite material of claim 1, as further described in claim 2 further comprising the steps of: adding an alcohol solvent to the reduction solution, wherein said addition of an alcohol solvent such as isopropyl alcohol and/or ethyl alcohol, helps expand the ionic polymer network and enhances deeper penetration of noble and none noble metal particles into said ionic polymer molecular network.

5. The manufacturing processes for the novel ionic polymer metal composite material of claim 1, as further described in claim 2 further comprising the steps of: mechanically stretching the said ionic polymer before the start of manufacturing processes described in claims **1**, **2**, **3** and **4**, wherein said mechanical stretching helps expand the ionic polymer network and enhances deeper penetration of noble and none noble metal particles into said ionic polymer molecular network.

6. The novel ionic polymer metal composite of claim 1 to be used as electromechanical sensors in the sense that if they are mechanically moved or deformed they generate an electrical voltage across their surface electrodes. Typical values are that for a cantilever sample of such active materials of dimensions 20 mm×5 mm×0.2 mm flipped at one end by 10 mm, generates up to 10 mV across its surface electrodes.

7. The novel ionic polymer metal composite of claim 1 to be used as electromechanical actuators, transducers and artificial muscles in the sense that if they are electrically activated by placing an electric field across their surface electrodes of the said cantilever sample in claim 6 as a bending actuator, they move or bend or flip dynamically like a wing with time varying electric fields. Typical values are that a cantilever sample of such active materials of dimensions 20 mm×5 mm×0.2 mm placed in an electric field of 5 mV/μm, generates a bending deflection of about 10 mm at its free end.

8. The novel ionic polymer metal composite material of claim 1 further encapsulated inside a flexible polymeric membrane to keep it hermetically sealed and moist and to provide additional outside protection.

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