Abstract: Described herein is an organic-inorganic hybrid compound comprising a salt of an organic cation with a polyoxometalate anion, comprising a stoichiometric ratio of organic cation to polyoxometalate anion. More specifically the following formulae (I) - (IV) describe the organic cations: Also described are methods of making an organic-inorganic hybrid compound; a precursor composition; methods of making a precursor composition; a nanocomposite proton-exchange membrane; methods of making a nanocomposite proton-exchange membrane; a membrane-electrode assembly; methods of making a membrane-electrode assembly; a fuel cell; and associated uses.
Technical field

The present invention relates generally to methods and materials for use in fuel cell applications, such as proton-exchange membranes and methods of their manufacture.

Background of the Invention

The operation of electrochemical devices requires the occurrence of oxidation and reduction reactions that are physically separated into compartments connected through conductors of charge carriers, which may be either electrons or ions. The two compartments are most commonly connected through an external electron conductor which conducts electrical current produced or consumed in the reactions, whereas electrolytes conduct ionic species between the two compartments and complete the electrochemical circuit needed for operation. A particular case of an ionically conducting electrolyte is a proton conducting electrolyte which is employed in devices such as fuel cells which require proton conduction in part of the electrochemical circuit. For electrolytes to perform their role they must be poor conductors of electrons.

Proton conducting electrolytes are commonly manufactured in the form of solid electrolytes as thin membranes known as proton exchange membranes (PEM). The advantages of using PEM in electrochemical devices such as fuel cells are numerous. A solid electrolyte is simpler and more compact than liquid electrolytes, has better mechanical properties that allow for thin membranes, and supports convenient manufacturing methods.

When using a PEM as an electrolyte in a fuel cell numerous properties are desired. These include: high ionic (such as proton) conductivity; zero conductivity of electrons; low gas and fuel permeability; resistance to swelling; minimal water transport; high resistance to dehydration, oxidation, reduction and hydrolysis; a high ion transport number; surface properties allowing easy catalyst bonding; and mechanical strength. In order to meet these requirements PEM usually consist of a polymer matrix containing functional groups or components capable of supporting the required properties.

The most widely and commercially used polymers for PEM manufacturing belong to a class of compounds known as perfluorosulfonic acids (PFSA) developed at DuPont and Dow Chemicals Company. These polymers are fully fluorinated, meaning that all sites that would be occupied by hydrogen atoms in a conventional hydrocarbon polymer have been replaced by fluorine atoms. This makes the polymers extremely resistant to chemical attack. The additional presence of sulfonic groups results in a specific morphology that supports proton conductivity.
PFSA polymers are generally synthesized by copolymerization of a derivatized, or active, comonomer with tetrafluoroethylene (TFE). After synthesis, the thermoplastic, hydrophobic and electrochemically inert polymer is converted into an ionomer in its salt form through basic hydrolysis. This can then be converted to the protonated form by ion-exchange with a strong acid, with the sulfonate groups (RSO3−) acting as the stationary counter charge to the mobile protons (H+).


Another type of polymer used for PEM in fuel cells is a derivatized trifluorostyrene (TFS) of the type developed by Ballard Advanced Materials. This polymer has a fully fluorinated backbone, but some of the side chains have hydrogen atoms. The polymer is synthesized by copolymerizing derivatized and non-derivatized trifluorostyrene monomers resulting in an electrochemically inactive thermoplastic. Non-derivatized monomers are then sulfonated to yield a proton conducting polymer.


Other homogeneous proton conducting polymers are also known. They generally consist of a variety of organic polymeric structures derivatized with sulfonic groups. Sulfonated polymers can have poor physical properties making them difficult to handle or, for example, can be susceptible to tearing or puncturing.
PEM manufactured from sulfonated polymers exhibit proton conductivities suitable for fuel cell operation when they are well hydrated, whereas in anhydrous form they exhibit negligible proton conductivities. High hydration levels generally result in significant swelling of the membrane. At ambient pressures and temperatures approaching the boiling point of water the hydration level of sulfonated polymers starts to decrease resulting in a substantial decrease in proton conductivity. The loss of water from the system renders the sulfonated polymer based PEM-containing device non-operational at temperatures between 80°C and 110°C. The temperature at which the PEM loses conductivity may be partially overcome by operation of the device at higher pressures or by incorporating hydrophilic components such as silica in the membrane. However, both solutions have serious limitations. In some applications, humidifying incoming reactant gas streams has been practiced in order to elevate the level of hydration in the PEM, however, humidifiers add to the cost and complexity of the system and increase parasitic power losses during operation. Humidifying becomes increasingly difficult at elevated temperatures. As a result, there is a need for proton-conducting materials that are capable of efficient proton transport with little or, ideally, no water.

In some applications, including some automotive applications, there is a desire to operate fuel cells at higher temperatures, i.e. above 100°C, preferably at temperatures above 135 °C or even in the range from 200°C to 300°C. Operation at elevated temperatures can simplify the cooling system while improving heat management and may result in higher efficiency of electrochemical reactions and possibly the use of the generated waste heat in combined heat and power systems. Operating at higher temperatures may also improve catalyst resistance to carbon monoxide poisoning when using reformed fuels or allow the use of non-noble metal electrode catalysts, thus reducing costs.

An alternate approach to developing homogeneous proton conducting membranes is to combine an electrochemically active or inactive polymer with a proton conductive additive or filler other than water. An example of such non-homogeneous, composite membranes is offered by membranes based on polybenzimidazole copolymers in which phosphoric acid is used as the filler to produce membranes capable of operating at temperatures up to 180°C without the need for humidification. A limitation of this particular solution is the tendency of phosphoric acid to leach from the membrane at low operating temperatures.

Among potential proton conducting polymer fillers one can also find heteropolyacids (HPA), which are characterized by some of the highest proton conductivities. These strongly hydrated inorganic compounds suffer from their high solubility in water, which can result in substantial leaching during fuel cell operation. Strategies for integration of HPA therefore focus on methods for anchoring HPA in polymer matrices. A comprehensive review of the state-of-the-art in the use of HPA in proton exchange fuel cells was recently published by Sachdeva et al. (Struct. Bond. 2011, 141, 115-168). Strategies to employ HPA in efficient PEM may be summarized into the following classes: a) HPA doped membranes, b) sol-gel based HPA membranes, and c) polypom membranes.
The current state-of-the-art concerning the use of HPA derivatives in fuel cells can be seen from recent literature.

US 6,864,006, US 6,680,138 and US 2004 0028978 (Honma et al.) propose proton conducting membranes employing ion conductors composed of heteropolycarboxylic acids as a proton conducting agent in conjunction with reagents containing hydrolysable silyl groups and amino groups. Bourlinos et al. (J. Am. Chem. Soc. 2004, 126, 15358-1 5359) report on polyoxometalates-based liquid salts containing quaternary ammonium cations that give medium ionic conductivity of \(6 \times 10^{-4}\) S/cm at 140°C and are proposed as an alternative for attaining anhydrous proton conduction. EP1 68561 8, (Kranz and Hoevar) proposes composite membranes that use a variety of electrochemically inert high-performance polymers with high chemical stability blended with ionic liquids, heteropolycarboxylic acids and silica to give membranes of medium conductivity. US 8,206,874, (Hamrock et al.) proposes PEM containing polyoxometalates or heteropolycarboxylic acids comprising transition metals Mn or Ce. Synthesized lacunary HPA were used to prepare organic-inorganic hybrid monomers that can be polymerized in a radical reaction to yield a polymer electrolyte. PEM and MEA were produced when this polymer electrolytes were combined with polymers that could be fluorinated and could contain acidic groups.

Ionic liquids, i.e. salts with low melting temperatures, generally below 100°C, are known to exhibit high ionic conductivity in the absence of water or solvents, high thermal stability, and a very low vapor pressure. Structurally, ionic liquids are salts comprised of organic cations, of which quaternary ammonium cations, N-substituted quaternary imidazolium cations, and quaternary pyridinium cations are most common. The charge is normally balanced by anions that are conjugate bases of strong acids.

These materials have also been explored as electrolytes for batteries and other devices, and also as ion conductors in PEM. Several proposals have been made for the use of ionic liquids as proton exchange materials mainly intended for use in fuel cells, which include the use of aprotic and protic ionic liquids. The proton conductivity cited in the examples was in the range of at most \(10^{-4}\) to \(10^{-5}\) S/cm without humidification thus necessitating a further improvement for utilization in PEM without humidification. In particular, ionic liquids were used to enhance proton conductivity in polymer blends. When blended with a polymer the ionic liquid can also act as a plasticizer or partial solvent at elevated temperatures. An example of the approach, combining a perfluorosulfonic polymer with ionic liquids is offered by Schmidt et al. (Chem. Eng. Technol. 2008, 31, 13-22).

However, materials prepared by impregnating a polymer material with an ionic liquid, suffer from a latent problem due to the leakage of the unbound ionic liquid. To address this problem, solid electrolytes were developed by increasing the molar mass of the ionic liquid. An example of this approach is the polymerization of a protic ionic liquid, a N-vinylimidazole salt, however, the proton conductivity of the resulting polymer was not at a satisfactory level and needed to be further improved.
A review of polymeric ionic liquids and their applications was published by Mecerreyes (Prog. Poly. Sci. 2011, 36, 1629-1648).

A proton conducting material and fuel cell using the same is presented by Hojo ef al. in US 8,211,590, wherein stable fuel cell functioning is alleged without humidification in the temperature range between room temperature to about 200°C. The proton conductivity is supported by heterocyclic organic compounds based on imidazole derivatives.

Honma ef al. (Electrochimica Acta 2008, 53, 7638) described an organic-inorganic crystalline electrolyte based on 12-phosphotungstic acid and an ionic liquid. The hybrid material was shown to be thermally stable up to 400°C and exhibited a high ion conductivity jump due to melting. At 240°C a conductivity of 1 × 10⁻² S/cm was reported. Similar hybrids with low melting temperatures were prepared by Rickert ef al. (J. Phys. Chem. B 2007, 111, 4685-4692) by pairing Keggin and Lindquist polyoxometalate anions with tetraalkylphosphonium cations.

The use of ionic liquids in proton exchange electrolytes shows promise due to inherent ion conductivity in the absence of water, however improved solutions that could support commercially interesting products are still being sought.


While the methods outlined above allegedly allow the fabrication of composite membranes that may present enhanced structural and thermal stability and ionic conductivity, the methods used do not allow the flexibility needed for fabricating composite membranes suitable for use in a wide range of applications. Thus there is a continuing need to look for electrolytes, proton exchange membranes, and membrane fabricating processes that allow greater flexibility in controlling the physical properties of the composite membranes.

**General Notes**

A number of patents and publications are cited herein in order to more fully describe and disclose the invention and the state of the art to which the invention pertains. Each of these references is incorporated herein by reference in its entirety into the present disclosure, to the same extent as if each individual reference was specifically and individually indicated to be incorporated by reference.
Throughout this specification, including the claims which follow, unless the context requires otherwise, the word "comprise" and variations such as "comprises" and "comprising," will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

It must be noted that, as used in the specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise.

Ranges may be expressed herein as from "about" one particular value, and/or to "about" another particular value. When such a range is expressed, another embodiment includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by the use of the antecedent "about," it will be understood that the particular value forms another embodiment.

This disclosure includes information that may be useful in understanding the present invention. It is not an admission that any of the information provided herein is prior art or relevant to the presently claimed invention, or that any publication specifically or implicitly referenced is prior art.

**Summary of the Invention**

It is an objective of the present invention to provide an improved proton-conducting membrane and, more particularly, to provide an improved method of fabricating said membranes and to provide composite membranes obtainable using such methods. In particular, the present invention seeks to improve on the current state-of-the-art by providing proton conducting electrolytes and proton exchange membranes that are capable of supporting fuel cell operation at temperatures between 195 and 300°C under operating conditions that do not include any form of humidification of the reagents or the device.

**Polvoxometalate Hybrid Compound**

A first aspect of the invention is an organic-inorganic hybrid compound comprising a salt of an organic cation with a polyoxometalate anion, comprising a stoichiometric ratio of organic cation to polyoxometalate anion.

The organic cation and the polyoxometalate anion have a stoichiometric ratio. "Stoichiometric ratio" refers to a ratio of organic cation to polyoxometalate anion which is charge-balanced. For example, where the charge on the anion is \((4^-)\) and the charge on the cation is \((1^+)\), a stoichiometric molar ratio of cations to anions would be \(4:1\). This means that the hybrid compound is free of impurities which would upset the charge balance resulting in a non-stoichiometric ratio of organic cation to polyoxometalate anion. The ionic salt is therefore of very high purity.
The stoichiometric compounds of the present invention display properties which make them suitable for use in fuel cell electrolytes such as proton exchange membranes. For example, the organic-inorganic hybrid compound is insoluble in water, which is crucial to the successful application of the compound in fuel cells where water is a common by-product. Furthermore, the compound is not hygroscopic and has a very high thermal stability. This allows the compound to be used in a proton conducting electrolyte which is operational between temperatures of 195°C and 300°C, which provides various advantages as described above.

The stoichiometric hybrid compounds of the present invention suitably exhibit a second-order phase transition at high temperature which leads to an ionic conductivity of between $10^{-3}$ S/cm and $10^{-2}$ S/cm which is sustainable across the whole temperature range of 195°C to 300°C. Such a high ionic conductivity at high temperature means that the compounds may be used to provide highly efficient proton exchange membranes and therefore highly efficient fuel cells.

In the organic-inorganic hybrid compound, the organic cation may be selected from one or more of substituted or unsubstituted imidazolium, substituted or unsubstituted pyridinium, quaternary ammonium, substituted or unsubstituted piperidinium and tetraalkyl phosphonium.

In the organic-inorganic hybrid compound, the organic cation may be defined according to any one of the following formulae:

\begin{align*}
\text{(I)} & & \text{(II)} & & \text{(III)} \\
\text{(IV)}
\end{align*}

wherein $R^1$ and $R^2$ are each independently saturated aliphatic C4-alkyl; $R^3$ is independently hydrogen, or linear or branched C4-alkyl; and $R^4$ and $R^5$ are each independently saturated aliphatic C$^4$-alkyl; $R^6$, $R^7$, $R^8$ and $R^9$ are each independently selected from linear or branched C5-alkyl; $R^{10}$ is independently
selected from aryl, heteroaryl, cycloaliphatic, alkenyl and alkynyl; and n is an integer within the range from 5 to 1000. Alkenyl and alkynyl groups may suitably be rigid.

Suitable R\textsuperscript{10} groups include optionally substituted or unsubstituted ethenyl, ethynyl, aryl, heteroaryl or cycloalkyl linker groups, e.g. \(-\text{CH}=\text{CH}-(\text{cis or trans}),\) phenylene (e.g. 1,4- or 1,3-phenylene) or pyridylene (e.g. 2,6-); the degree of polymerisation - n, of the polymeric salt may be sufficiently large that the salt is insoluble in water. The degree of polymerisation - n is an integer within the range from 5 to 1000. (see J.Y. Ying, Y. Zhang, D. Hu, P.K. Patra, Polymeric salts and poly-NHC-metal complexes, US 8,163,851 B2).

In some embodiments, the organic cation is not 1-butyl-3-methylimidazolium.

Such cations or quaternary pyridinium cations (Py) provide formation of water insoluble salts with polyoxometalate anions that exhibit substantial proton conductivity within the range of around 1 to around 50 mS/cm at elevated (below 100 °C) or high temperatures (over 100 °C and up to 300 °C). Proton transport between the protonated Py or Im (HPy\textsuperscript{+} or HIm\textsuperscript{+}) and neat Py or Im (the proton defects, i.e., vacant nitrogen site of Py or Im) plays an important role for intermolecular proton transfer, and at an optimum composition enhances the proton conduction by Grothuss mechanism (see Kreuer, K. D.; Fuchs, A.; Ise, M.; Spaeth, M.; Maier, J. Electrochim. Acta 1998, 43, 1281).

The structure of 1-butyl-3-methylimidazolium (BMIM) is as follows:

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviation</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Butyl-3-methylimidazolium</td>
<td>BMIM</td>
<td><img src="image" alt="Structure" /></td>
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</tbody>
</table>

The organic cation may be selected from DMIM, EMIM, TMIM, NBMP, THTDP and PIM.

The full IUPAC names and structures of these organic cations is as follows:

<table>
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<tr>
<th>Name</th>
<th>Abbreviation</th>
<th>Structure</th>
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<tbody>
<tr>
<td>Name</td>
<td>Abbreviation</td>
<td>Structure</td>
</tr>
<tr>
<td>--------------------------------------------------</td>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>1,3-Dimethylimidazolium</td>
<td>DMIM</td>
<td><img src="https://example.com/dmim.png" alt="Structure" /></td>
</tr>
<tr>
<td>1,2,3-Trimethylimidazolium</td>
<td>TMIM</td>
<td><img src="https://example.com/tmim.png" alt="Structure" /></td>
</tr>
<tr>
<td>1-Ethyl-3-methylimidazolium</td>
<td>EMIM</td>
<td><img src="https://example.com/emim.png" alt="Structure" /></td>
</tr>
<tr>
<td>N-Butyl-4-methylpyridinium (1-Butyl-4-methylpyridinium)</td>
<td>NBMP</td>
<td><img src="https://example.com/nbmp.png" alt="Structure" /></td>
</tr>
<tr>
<td>Trihexyltetradecylphosphonium</td>
<td>THTDP</td>
<td><img src="https://example.com/thtdp.png" alt="Structure" /></td>
</tr>
</tbody>
</table>
These particular cations provide salts when reacted with polyoxometalate anions which have a higher stability and exhibit an increased ionic conductivity. Furthermore, these salts are insoluble in water, which reduces the risk of leaching of the salt from a proton exchange membrane during use.

The polyoxometalate anion may be an isopolyoxometalate or a heteropolyoxometalate comprising a transition metal atom selected from W, V, Mo, Nb, Mn and Ce.

This includes a wide range of polyoxometalate structures that have different physico-chemical properties and may or may not be centrosymmetric. This class of superacids allows for a change of anion charge (most commonly 3-, 4- and 5-) and symmetry by the choice of metal ions in their structures. In turn these properties define the number of interacting 1+ charged organic cations and their distribution around the anion and consequently the molecular dynamics that governs conductivity. The polyoxometalate anions differ from other types of anions hitherto used in ionic liquids by their large size, which is in general larger than 1 nm. The centrosymmetric character of some polyoxometalate anions leads to delocalization of negative charge over the surface of this relatively large structure.

The polyoxometalate anion may be selected from silicotungstate and phosphotungstate. These two anions are among the most common and widely used polyoxometalate anions, especially the phosphotungstate anion the synthesis of which is relatively simple starting from tungsten oxide and phosphoric acid. Besides, these two anions are centrosymmetric with negligible polarity, which renders them soluble when in the form of acids or salts in non-polar organic solvents.

Silicotungstate has the formula \([\text{W}_{12}\text{S}_{10}\text{O}_{40}]^{4-}\) and may be more conveniently denoted \([\text{SiW}]^{4-}\). Phosphotungstate has the formula \([\text{PW}_{12}\text{O}_{40}]^{3-}\) and may be more conveniently denoted \([\text{PW}]^{3-}\).

Method of Making the Polyoxometalate Hybrid Compound

A second aspect of the invention is a method of making an organic-inorganic hybrid compound comprising the steps of,

- mixing a heteropolyacid with an organic salt comprising an organic cation and a counter anion,
- wherein the organic-inorganic hybrid compound formed comprises a stoichiometric ratio of organic cation to polyoxometalate anion.
The term "organic salt" refers to a salt containing an organic cation. The identity of the anion is not particularly limited.

The organic salt may be an ionic liquid. Ionic liquids generally possess low melting points. The ionic liquid may be miscible in water.

The method may be carried out by mixing the heteropolyacid and organic salt reactants in their pure form. Alternatively, they may be present in solution or in suspension.

Preferably, the heteropolyacid is a stronger acid than the acid of which the counter anion is a conjugate base. This results in an efficient ion exchange reaction wherein the conjugate base of the HPA replaces the conjugate base of the organic salt to produce a stoichiometric (charge balanced) organic-inorganic hybrid compound.

Heteropolyacids (HPA) are compounds made up of a metal, oxygen, a p-block element and acidic hydrogen atoms. Polyoxometalate anions are the conjugate bases of HPAs, i.e. HPAs undergo deprotonation to form polyoxometalate anions.

This general ion exchange reaction produces an organic-inorganic hybrid compound of stoichiometric composition; that is the combined charge of the organic cations matches exactly the charge of the polyoxometalate anion, regardless of any excess of reagent used.

The HPA is preferably silicotungstic acid (H4W12Si04o) or phosphotungstic acid (H3PW12O40).

The reaction product may be washed with a solvent in which the organic-inorganic hybrid compound is insoluble, but in which other species present in the reaction mixture are soluble.

The washing solvent may be water. The organic-inorganic hybrid compound formed in the method is generally insoluble in water, so a further step of washing with water removes impurities such as residual unreacted reactants to leave the pure stoichiometric product.

The further step of recrystallization of the organic-inorganic hybrid compound may be performed.

The organic cation may be selected from DMIM, EMIM, TMIM, NBMP, THTDP and PIM.

The counter anion in the organic salt may be chloride, bromide, iodide, tetrafluoroborate, hexafluorophosphate, trifluoroacetate, methylsulfate, trifluoromethanesulfonate or trifluoromethanesulfonimide.

The organic salt may be insoluble in water.
A further step of activation may be carried out alongside the existing method steps. The activation step may include heating and/or ultrasonic mixing.

A third aspect of the invention is an organic-inorganic hybrid compound produced by a method according to the second aspect.

Precursor Composition for a Proton Exchange Membrane
A fourth aspect of the invention is a precursor composition comprising,

- a polymer component;
- an organic salt comprising
  - a polyoxometalate anion and an organic cation, or
  - an organic-inorganic hybrid compound according to the first aspect; and
  - a compatible solvent.

The organic cation may be selected from DMIM, EMIM, TMIM, NBMP, THTDP and PIM.

The polyoxometalate anion may be an isopolyoxometalate or a heteropolyoxometalate comprising a transition metal atom selected from W, V, Mo, Nb, Mn and Ce.

The polyoxometalate anion may be selected from silicotungstate and phosphotungstate.

The organic salt may be present in the precursor composition in nanoparticulate form.

The term "nanoparticulate", "nanoparticle", "nanocrystal" or similar denotes particles wherein the size of the longest dimension is within the range of 1 to 100 nm. Suitably, "nanoparticulate" organic salts have a particle size not larger than 10 nm, for example 2 nm to 10 nm, for example 6 to 8 nm. When the organic salt takes nanoparticulate form in the precursor composition, improved properties of the resultant membrane made using the precursor composition are observed. Even in the case of high salt concentration in the membrane (e.g. 80 wt.%) it remains elastic (e.g. does not break at high curvature), translucent (e.g. no opalescence present) and can be prepared very thin (e.g. with thickness below 30 μm). Some membranes are hydrophobic, therefore they do not swell in the presence of water and are dimensionally stable in all three dimensions.

The organic salt may be present in an amount of up to 90, 80, 70, 60, 50, 40, 30 or 20 wt% of the sum of polymer component and salt component.

The organic salt may be present in an amount of at least 10 wt% of the total weight of polymer component and organic salt.
The organic salt may be present in an amount of from 10 to 90 wt% of the total weight of polymer component and organic salt.

The polymer component may comprise a single polymer or copolymer, or a mixture comprising one or more polymers and/or one or more copolymers.

The polymer component may comprise a chemically resistant organic polymer or copolymer.

The polymer component may comprise a conducting polymer or copolymer. Alternatively, a non-conducting polymer or copolymer may be used.

The polymer component may comprise one or more fluorinated polymers or copolymers.

The polymer component may comprise a polymer or copolymer which contains acidic or basic functional groups.

The polymer component may be present in an amount of at least 10 wt% of the total weight of polymer component and organic salt, for example at least 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 wt%.

The polymer component may be present in an amount of up to 70 wt% of the total weight of polymer component and organic salt, for example up to 69, 68, 67, 66, 65, 64, 63, 62, 61 or 60 wt%.

The term "compatible solvent" denotes a solvent which allows for the miscibility of the polymer and the organic salt such that the salt becomes dispersed through the polymer component.

The precursor composition may comprise a homogeneous mixture of the polymer component and the organic salt.

The compatible solvent may comprise a solvent selected from dimethylformamide, dimethylacetamide, dimethylsulfoxide, N-ethylpyrrolidine and N-methyl-2-pyrrolidone.
The compatible solvent may be present in an amount of at least 60 wt%, for example at least 61, 62, 63, 64, 65, 66, 67, 68, 69 or 70 wt% of the precursor composition.

The compatible solvent may be present in an amount of up to 90 wt%, for example up to 89, 88, 87, 86, 85, 84, 83, 82, 81 or 80 wt% of the precursor composition.

The compatible solvent may be present in an amount of between 65 and 75 wt% of the precursor composition.

The precursor composition may include an inorganic filler. The inorganic filler may be in the form of nanometre and/or micrometre sized solid particles.

The precursor composition may include one or more inorganic fillers selected from silicon dioxide, aluminium oxide, titanium oxide, montmorillonite clays and derivatives thereof.

The inorganic fillers may be generated in situ. The in situ generation may be from filler precursors including organic esters of orthosilicic acid. The inorganic fillers may be formed at any stage as long as the solvent is present. The inorganic filler particles may be nanoparticulate.

The precursor composition may include a processing aid component. The processing aid component may include a surfactant. The processing aid component may be present in an amount of from 0 to 4 wt% of the precursor composition.

Method of Making a Precursor Composition

A fifth aspect of the invention is a method of making a precursor composition, comprising the steps of, combining a polymer component with a proton conducting component in the presence of a compatible solvent;

wherein the proton conducting component is an organic salt comprising

an organic cation and a polyoxometalate anion, or

an organic-inorganic hybrid compound according to the first aspect; and

mixing to produce a homogeneous composition.

The organic cation may comprise a cation selected from DMIM, EMIM, TMIM, NBMP, THTDP and PIM.

The polyoxometalate anion may be an isopolyoxometalate or a heteropolyoxometalate comprising a transition metal atom selected from W, V, Mo, Nb, Mn and Ce.

The polyoxometalate anion may be selected from silicotungstate and phosphotungstate.
The organic salt may be present in nanoparticulate form. Suitably, "nanoparticulate" organic salts have a particle size not larger than 10 nm, for example 2 nm to 10 nm, for example 6 to 8 nm.

The proton conducting component may be synthesized in situ in the presence of the polymer.

The organic salt may be present in an amount of up to 90, 85, 80, 75, 70, 65, 60, 55 or 50 wt% of the total weight of polymer component and proton conducting component.

The organic salt may be present in an amount of at least 10 wt% of the total weight of polymer component and proton conducting component, for example at least 15, 20, 25, 30 or 35 wt%.

The organic salt may be present in an amount of from 10 to 90 wt% of the total weight of polymer component and proton conducting component.

The organic salt may be present in an amount of from 30 to 50 wt% of the total weight of polymer component and proton conducting component.

The polymer component may comprise a single polymer or copolymer, or a mixture comprising one or more polymers and/or one or more copolymers.

The polymer component may comprise a chemically resistant organic polymer or copolymer.

The polymer component may comprise a conducting polymer or copolymer. Alternatively, a non-conducting polymer or copolymer may be used.

The polymer component may comprise one or more fluorinated polymers or copolymers.

The polymer component may comprise a polymer or copolymer which contains acidic or basic functional groups.

The polymer component may comprise a polymer selected from polysulfone, polyethersulfone, polyphenylenesulfone, polyimide, polyimideamide, polyetherimide, polyetheretherketone, polyvinylidene fluoride and derivatives thereof.

The composition of the precursor composition may be adapted by choosing a particular polymer or combination of polymers and a particular solvent or combination of solvents in such a way as to obtain a precursor composition with rheological properties suitable for diverse technological methods of membrane production (continuous or discontinuous) and requiring different thermal treatment.
The polymer component may be present in an amount of at least 10 wt% of the total weight of polymer component and proton conducting component, for example at least 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 wt%.

The polymer component may be present in an amount of up to 70 wt% of the total weight of polymer component and proton conducting component, for example up to 69, 68, 67, 66, 65, 64, 63, 62, 61 or 60 wt%.

The polymer component may be present in an amount of from 50 to 65 wt% of the total weight of polymer component and proton conducting component.

The term "compatible solvent" denotes a solvent which allows for the miscibility of the polymer and the organic salt such that the salt becomes dispersed through the polymer component.

The precursor composition may comprise a homogeneous mixture of the polymer component and the organic salt.

The compatible solvent may comprise a solvent selected from dimethylformamide, dimethylacetamide, dimethylsulfoxide, N-ethylpyrrolidine and N-methyl-2-pyrrolidone.

The compatible solvent may be present in an amount of at least 60 wt%, for example at least 61, 62, 63, 64, 65, 66, 67, 68, 69 or 70 wt% of the precursor composition.

The compatible solvent may be present in an amount of up to 90 wt%, for example up to 89, 88, 87, 86, 85, 84, 83, 82, 81 or 80 wt% of the precursor composition.

The compatible solvent may be present in an amount of from 65 to 75 wt% of the precursor composition.

The precursor composition may include an inorganic filler. The inorganic filler may be in the form of nanometre and/or micrometre sized solid particles.

The precursor composition may include one or more inorganic fillers selected from silicon dioxide, aluminium oxide, titanium oxide, montmorillonite clays and derivatives thereof.

The inorganic fillers may be generated in situ. The in situ generation may be from filler precursors including organic esters of orthosilicic acid.
The precursor composition may include a processing aid component. The processing aid component may include a surfactant. The processing aid component may be present in an amount of from 0 to 4 wt% of the precursor composition.

A sixth aspect of the invention is a precursor composition made by the method according to the fifth aspect.

**Nanocomposite Proton Exchange Membrane**

A seventh aspect of the invention is a nanocomposite proton-exchange membrane, comprising,

- a polymer matrix comprising a polymer; and
- polyoxometalate nanoparticles embedded within the polymer matrix, the nanoparticles comprising
  - an organic cation and a polyoxometalate anion, or
  - an organic-inorganic hybrid compound according to the first aspect.

The term "nanoparticles" denotes particles wherein the size of the longest dimension of a particle is within the range of 1 to 100 nm. Suitably, the nanoparticles have a particle size not larger than 10 nm, for example 2 nm to 10 nm, for example 6 to 8 nm. As a result of the proton conducting polyoxometalate particles being nanoparticulate, the membrane has highly desirable properties such as:

- high elasticity even in the case of high salt concentration in the membrane (e.g. 80 wt.%);
- transparency (e.g. no opalescence present);
- can be prepared very thin (e.g. below 30 µm);
- low swelling or non-swelling;
- dimensional stability in all three dimensions.

The proton exchange membrane (PEM) according to the present invention may be employed as a proton-conducting electrolyte in an electrochemical device, such as a fuel cell. The membrane is placed between the anode and cathode in the device.

The polyoxometalate nanoparticles may comprise an organic-inorganic hybrid compound according to the first aspect. When the nanoparticles comprise such a compound the advantages discussed above in relation to the compound are imparted to the membrane itself, for example the insolubility of the compound ensures that leaching is minimised during use of the membrane. Furthermore, the high thermal stability which allows the membrane to operate efficiently at temperatures between 195°C and 300°C is advantageous when the membrane is used in a fuel cell. The high ionic conductivity exhibited by the compound is beneficial in an electronic device where the conductivity of the electrolyte dictates the efficiency of the device.
The nanoparticles may be homogeneously dispersed through the membrane.

The organic cation may be selected from DMIM, EMIM, TMIM, NBMP, THTDP and PIM.

5 The polyoxometalate anion may be an isopolyoxometalate or a heteropolyoxometalate comprising a transition metal atom selected from W, V, Mo, Nb, Mn and Ce.

The polyoxometalate anion may be selected from silicotungstate and phosphotungstate.

10 The polyoxometalate nanoparticles may be present in an amount of at least 10 wt% of the total dry membrane weight, for example at least 15, 20, 25 or 30 wt%.

The polyoxometalate particles may be present in an amount of up to 90 wt% of the total dry membrane weight, for example up to 85, 80, 75, 70, 65, 60, 55, 50 or 45 wt%.

15 The polyoxometalate nanoparticles may make up between 10 and 90 wt% of the total dry membrane weight.

The polyoxometalate nanoparticles may make up between 30 and 50 wt% of the total dry membrane weight.

The polymer matrix may comprise a single polymer or copolymer, or a mixture comprising one or more polymers and/or one or more copolymers.

20 The polymer matrix may comprise a chemically resistant organic polymer or copolymer.

The polymer matrix may comprise a conducting polymer or copolymer. Alternatively, a non-conducting polymer or copolymer may be used.

25 The polymer matrix may comprise one or more fluorinated polymers or copolymers.

The polymer matrix may comprise a polymer or copolymer which contains acidic or basic functional groups.

30 The polymer may be selected from polysulfone, polyethersulfone, polyphenylenesulfone, polyimide, polyimideamide, polyetherimide, polyetheretherketone, polyvinylidene fluoride and derivatives thereof.

35 The polymer may be present in an amount of at least 10 wt% of the total dry membrane weight, for example at least 15, 20, 25, 30, 35, 40, 45 or 50 wt%.
The polymer may be present in an amount of up to 90 wt% of the total dry membrane weight, for example up to 85, 80, 75, 70 or 65 wt%.

The polymer may make up between 10 and 90 wt% of the total dry membrane weight.

The polymer may make up between 55 and 65 wt% of the total dry membrane weight.

The membrane may include an inorganic filler. The inorganic filler may be in the form of nanometre and/or micrometre sized solid particles.

The inorganic filler may make up between 5 and 60 wt% of the total dry membrane weight.

The membrane may include one or more inorganic fillers selected from silicon dioxide, aluminium oxide, titanium oxide, montmorillonite clays and derivatives thereof.

The inorganic fillers may be generated in situ during membrane formation. The in situ generation may be from filler precursors including organic esters of orthosilicic acid.

The membrane may have a thickness of at least 10 µm, for example at least 20, 30, 40, 50, 60 or 70 µm.

The membrane may have a thickness of up to 500 µm, for example up to 450, 400, 350, 300, 250, 200, 150 or 100 µm. The membrane may have a thickness of up to 95, 90, 85 or 80 µm.

The membrane may have a thickness of from 10 to 500 µm.

The result is a proton exchange membrane suitable for use as the electrolyte in a fuel cell which can operate in a wide high-temperature range of 80-300°C. Existing HT PEMFCs cannot cover this range of temperatures. Furthermore, the membrane is not prone to leaching of the proton conducting component. Additionally, the presence of water is not required for the operation of a HT PEMFC comprising the membrane - no gas humidification or water management of the electrolyte is required.

At the high temperatures possible, the H₂-rich fuel may contain a substantial concentration of carbon monoxide and low concentration of sulphur compounds without causing damage to the fuel cell.

Method of Making a Nanocomposite Proton Exchange Membrane

An eighth aspect of the invention is a method of making a nanocomposite proton-exchange membrane, comprising the steps of,

applying the precursor composition according to the fourth aspect, or a precursor composition made by a method according to the fifth aspect, to a substrate, or
applying a melt comprising the organic-inorganic hybrid compound according to the first aspect and a polymer to a substrate; and optionally drying to produce a membrane.

"Drying", in the case of a membrane made from the precursor composition, means for example allowing the solvent to evaporate to leave the dry membrane, which may include heating the applied composition.

"Drying", in the case of a membrane formed from the melt, means for example allowing the applied melt to cool and solidify to produce the dry membrane.

When the precursor composition is applied to the substrate, drying may be performed to drive off the solvent present in the precursor composition and leave the polymer matrix with embedded polyoxometalate nanoparticles. Because of the compatible solvent which produces a dispersion of nanoparticles through the polymer component of the precursor composition, as the solvent is driven off and the precursor composition dries to produce the membrane the nanoparticles are correspondingly dispersed through the polymer matrix of the membrane. This may be a homogeneous dispersion.

The dispersed nanoparticles of polyoxometalate salt are immobilised within the proton exchange membrane structure through entrapment in the polymer matrix.

Immobilisation in the polymer matrix may be through mechanisms including precipitation as an insoluble salt, or non-covalent or covalent attachment to a component of the blend.

Such trapping of the polyoxometalate nanoparticles means that leaching of the salt during operation of an electrical device incorporating the membrane as an electrolyte is reduced, or prevented.

When the melt is used to form the membrane, the melt is prepared by heating a mixture of the components to above the melting point of the polymers and homogenised by mixing, before being cast onto the substrate. Again, the homogeneity is reflected in the structure of the dry membrane.

The precursor composition or melt may be applied to the substrate by blade application, calendering, dip coating or spin coating.

The substrate may be glass.

The method may further include the step of cooling the membrane after drying.
The method may further include the step of rinsing the membrane with distilled water after drying or after cooling.

The method may further include the step of detaching the membrane from the substrate after drying or after cooling or after rinsing.

The polymer may be selected from polysulfone, polyethersulfone, polyphenylenesulfone, polyimide, polyamideimide, polyetherimide, polyetheretherketone, polyvinylidene fluoride and derivatives thereof.

A ninth aspect of the invention is a nanocomposite proton-exchange membrane made by the method according to the eighth aspect.

Membrane-Electrode Assembly
A tenth aspect of the invention is a membrane-electrode assembly comprising,

c a nanocomposite proton-exchange membrane according to the seventh aspect, or a nanocomposite proton-exchange membrane made by a method according to the eighth aspect, between two gas diffusion electrodes.

The membrane according to the seventh aspect or produced according to the eighth aspect may thus be used as a proton conducting separator in an electrochemical device. For example, such a membrane may be used in a fuel cell where it may be placed between the anode and the cathode.

The gas diffusion electrodes (GDE) are placed one on each side of the membrane. One GDE may be the anode while the other is the cathode. The GDEs allow fuel and oxidant to reach a catalyst.

Method of Making a Membrane-Electrode Assembly
An eleventh aspect of the invention is a method of making a membrane-electrode assembly comprising the steps of,

attaching a first gas diffusion electrode to a first surface and a second gas diffusion electrode to a second surface of the membrane according to the seventh aspect, or the membrane made by a method according to the eighth aspect.

The membrane-electrode assembly (MEA) so produced, when inserted into a fuel cell and supplied with fuel and an oxidant, will function to produce electrical potential and current between the GDEs which can be employed through an external part of the electrical circuit as a power source.

A precursor composition according to the fourth aspect, or a composition made by a method according to the fifth aspect, may be applied to an inner surface of the first gas diffusion electrode and/or the second gas diffusion electrode before attachment to the membrane. The inner surface is the surface of the GDE adjacent the membrane.
One or more of heat and pressure may be applied during attachment of the gas diffusion electrodes.

The method may include the step of application of a catalyst to the first surface of the membrane and/or application of a catalyst to the second surface of the membrane, before attachment of the GDEs.

The catalyst applied to the first side of the membrane may be the same as or different to the catalyst applied to the second side. The catalysts may be different due to the different electrochemical reactions occurring at the anode and cathode.

The catalyst may be a classical Pt/C catalyst or Pt-transition metal(s) alloyed catalyst supported on graphitised carbon, or Pt-skin nanoparticle catalyst supported on various electrically conductive supports.

The catalyst may be applied to a membrane, cured or uncured, by a method well known to those skilled in the art, such as decal pressure, spray application or printing to obtain catalyst-coated membranes (CCM).

A twelfth aspect of the invention is a method of making a membrane-electrode assembly comprising the steps of,

applying a precursor composition according to the fourth aspect, or a composition made by a method according to the fifth aspect, to the inner surface of a first gas diffusion electrode; and attaching a second gas diffusion electrode to the applied composition.

A step of drying the composition may take place either before the attachment of the second GDE or after the attachment of the second GDE. Where drying takes place before such attachment, the second GDE is attached to the dried membrane. Where drying takes place after such attachment, the second GDE is attached to the precursor composition which subsequently dries to form the membrane.

A thirteenth aspect of the invention is a membrane-electrode assembly made by a method according to the eleventh aspect or by a method according to the twelfth aspect.

**Fuel Cell**

A fourteenth aspect of the invention is a fuel cell comprising the membrane-electrode assembly according to the tenth aspect, or a membrane electrode assembly made by a method according to the eleventh aspect or by a method according to the twelfth aspect.
A fifteenth aspect of the invention is use of a nanocomposite proton-exchange membrane according to the seventh aspect, or a membrane made by a method according to the eighth aspect, as a proton-conducting electrolyte in a fuel cell.

**Brief Description of the Drawings**

Figure 1 shows the mass balance of the ion exchange reaction between silicotungstic acid and an imidazolium chloride ionic liquid carried out in distilled water at different ionic liquid additions to a constant quantity of the HPA. Open squares depict the mass of reagents remaining in solution and filled squares depict the mass of the insoluble reaction product.

Figure 2 shows the crystal structure of the ion pair formed by the reaction of phosphotungstic acid hydrate and 1-butyl-3-methyl imidazolium hexafluorophosphate (BMIMPF6). The 3- negative charge of the phosphotungstate anion is balanced by 3 imidazolium cations each carrying a 1+ charge.

Figure 3 shows a thermal gravimetric analysis scan giving the relative mass loss in dependence of temperature for a representative organic-inorganic ion pair made by reacting silicotungstic acid and BMIMCl. The ion pair shows stability past 376°C while the differential thermal analysis plot shows a transition at 194°C.

Figure 4 shows a representative conductivity vs. reciprocal temperature diagram obtained from impedance spectroscopy measurements in dry helium of an organic-inorganic ion made by reacting silicotungstic acid and BMIMCl. The diagram indicates that conductivities above 10⁻³ S/cm are achieved above the temperature of the second order transition and that a hysteresis takes place under the used measurement conditions.

Figure 5 shows a representative differential scanning calorimetry (DSC) scan with two heating curves and one cooling curve for the ion pair formed from silicotungstic acid and BMIMCl. The peaks mark heat flows attributed to a reversible second order transition.

Figure 6 shows two pairs of polarization and power curves: one measured at 250°C in a 12 cm² single cell on a MEA manufactured through the methods described in this disclosure, Example 16C, employing dry hydrogen and ambient air as fuel and oxidant, respectively, and the other measured at 195°C in a 25 cm² single cell on the MEA with the same composition but employing dry hydrogen and oxygen as fuel and oxidant, respectively.

Figure 7 shows (a) view along the \( a \)-axis of the structure of the salt produced in Example 7, as determined by single-crystal X-ray crystallography, and (b) a view of the crystalline structure of the same salt along the \( c \)-axis.
Figure 8 shows a view of the same crystalline structure as shown in Figure 7, but along the c-axis.

Figure 9 shows polarization curves for the MEA produced in Example 16.

Figure 10 shows the polarization curve for the MEA produced in Example 17.

Figure 11 shows the polarization curve for the MEA produced according to Example 18.

Figure 12 shows the polarization curve for the MEA produced according to Example 19.

Figure 13 shows (a) an assembled MEA according to one embodiment of the present invention, and (b) an exploded perspective view of the same MEA where the proton conducting membrane is visible.

Figure 14 shows an exploded perspective view of a fuel cell according to one embodiment of the present invention.

Figure 15 shows a photograph of a membrane, electrodes and an MEA according to one embodiment of the present invention.

**Detailed Description**

Any sub-titles herein are included for convenience only, and are not to be construed as limiting the disclosure in any way.

The invention will now be further described with reference to the following non-limiting Figures and Examples. Other embodiments of the invention will occur to those skilled in the art in the light of these.

The disclosure of all references cited herein, inasmuch as it may be used by those skilled in the art to carry out the invention, is hereby specifically incorporated herein by cross-reference.

The organic-inorganic hybrid compounds of the present invention comprise a stoichiometric ratio of organic cation to polyoxometalate anion. In other words, the compounds are of high purity, with little or no contamination within the ionic structure of the salt. The proton exchange membranes according to the present invention are operational within a temperature range of 195-300°C, and it is therefore important that the polyoxometalate salt is stable and exhibits high ionic conductivity within this temperature range. An ionic conductivity of at least $10^{-3}$ S/cm is desirable in order for satisfactory efficiency of a PEM to be achieved. The polyoxometalate salts of the present invention achieve both increased stability and ionic conductivity due to their stoichiometric structure, thereby providing a material which is used to produce PEMs which are more efficient and stable.
The organic-inorganic hybrid compounds of the present invention are insoluble in water and are thus resistant to leaching under fuel cell operating conditions that generally involve the formation and transport of water through one or more components of the device or the device as a whole. The compounds are soluble in organic solvents of different dielectric constants such as for example dimethyl formamide.

The organic-inorganic hybrid compounds can be synthesized through a reaction in which the conjugate anion of the stronger acid replaces the conjugate anion of a weaker acid. A convenient method for the synthesis of said ion pairs is to combine a heteropolyacid - a polyoxometalate anion that has its negative charge neutralized by a stoichiometric number of protons - with a salt of the organic cation that will combine with the polyoxometalate anion in a new ion pair. The counterion to the organic cation can be, but is not limited to, any of the following anions: chloride, bromide, iodide, tetrafluoroborate, hexafluorophosphate, trifluoroacetate, methylsulfate, trifluoromethanesulfonate or trifluoromethanesulfonimide. Such salts generally possess low melting points and are therefore known as ionic liquids. The type of anion generally determines the miscibility of the ionic liquid with water but does not influence the formation and composition of the ion pair if the condition is met that the anion is a conjugate ion of an acid that is weaker than the heteropolyacid used in the reaction. The metathesis reaction may be carried out through mixing of the reagents in pure form, in suspension or in solution. At least one reagent may be in liquid form either as a pure compound or in solution or suspension. The reaction may require heating, ultrasonic mixing or other methods of activation.

The organic-inorganic hybrid salts may be prepared from water soluble as well as water insoluble ionic liquids. "Ionic liquid" refers to an ionic compound with a low melting point, for example below 100°C.

When the salt synthesis is carried out in the presence of less polar or non-polar organic solvents (in which the polyoxometalate acid must be soluble), water insoluble ionic liquids are preferred for a more efficient reaction.

The organic-inorganic hybrid compounds of the present invention may be prepared from the reaction of an ionic liquid with a heteropolyacid. The heteropolyacid may be silicotungstic acid or phosphotungstic acid, having the formulae H₄SiW₁₂O₴₀ and H₃PW₁₂O₴₀ respectively. Examples of some possible ionic liquids which may be reacted with either of the above heteropolyacids to produce suitable polyoxometalate organic-inorganic hybrids are given in the table below. The chemical structures of the DMIM, EMIM, TMIM, NBMP, THTDP and PIM cations are provided above.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>[DMIM]Cl</td>
</tr>
<tr>
<td>B</td>
<td>[DMIM]Br</td>
</tr>
<tr>
<td>C</td>
<td>[DMIM]I</td>
</tr>
<tr>
<td>Compound</td>
<td>Structure</td>
</tr>
<tr>
<td>----------</td>
<td>----------------</td>
</tr>
<tr>
<td>D</td>
<td>[DMIM]BF₄</td>
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<tr>
<td>E</td>
<td>[DMIM]PF₆</td>
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<tr>
<td>F</td>
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</tr>
<tr>
<td>G</td>
<td>[DMIM]CF₃SO₃</td>
</tr>
<tr>
<td>H</td>
<td>[DMIM]CH₃SO₄</td>
</tr>
<tr>
<td>I</td>
<td>[DMIM]NS₂O₄C₂F₆</td>
</tr>
<tr>
<td>J</td>
<td>[EMIM]Cl</td>
</tr>
<tr>
<td>K</td>
<td>[EMIM]Br</td>
</tr>
<tr>
<td>L</td>
<td>[EMIM]I</td>
</tr>
<tr>
<td>M</td>
<td>[EMIM]BF₄</td>
</tr>
<tr>
<td>N</td>
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<tr>
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<td>[EMIM]CF₃SO₃</td>
</tr>
<tr>
<td>Q</td>
<td>[EMIM]CH₃SO₄</td>
</tr>
<tr>
<td>R</td>
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</tr>
<tr>
<td>S</td>
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</tr>
<tr>
<td>T</td>
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<td>W</td>
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<tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>[THTDP]Br</td>
</tr>
<tr>
<td>AM</td>
<td>[THTDP]I</td>
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<tr>
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<td>[THTDP]BF₄</td>
</tr>
<tr>
<td>AO</td>
<td>[THTDP]PF₆</td>
</tr>
</tbody>
</table>
(NS$_2$O$_4$F$_6$) represents the bis(trifluoromethanesulfonyl)amide anion.

Thus the following organic-inorganic hybrid compounds are some of the possible compounds which may be formed in the method of the present invention.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP</td>
<td>[THTDP]CO$_2$CF$_3$</td>
</tr>
<tr>
<td>AQ</td>
<td>[THTDP]CF$_3$SO$_3$</td>
</tr>
<tr>
<td>AR</td>
<td>[THTDP]CH$_3$SO$_4$</td>
</tr>
<tr>
<td>AS</td>
<td>[THTDP]NS$_2$O$_4$C$_2$F$_6$</td>
</tr>
<tr>
<td>AT</td>
<td>[PIM]Cl</td>
</tr>
<tr>
<td>AU</td>
<td>[PIM]Br</td>
</tr>
<tr>
<td>AV</td>
<td>[PIM]I</td>
</tr>
<tr>
<td>AW</td>
<td>[PIM]BF$_4$</td>
</tr>
<tr>
<td>AX</td>
<td>[PIM]PF$_3$</td>
</tr>
<tr>
<td>AY</td>
<td>[PIM]CO$_2$CF$_3$</td>
</tr>
<tr>
<td>AZ</td>
<td>[PIM]CF$_3$SO$_3$</td>
</tr>
<tr>
<td>BA</td>
<td>[PIM]CH$_3$SO$_4$</td>
</tr>
<tr>
<td>BB</td>
<td>[PIM]NS$_2$O$_4$C$_2$F$_6$</td>
</tr>
</tbody>
</table>

The organic-inorganic hybrid compounds of the present invention undergo a phase-transition associated with a large step up in conductivity. This is observed for salts prepared by methods which use both soluble and insoluble ionic liquids as reactant.
The melting points of the organic-inorganic hybrid compounds according to the present invention fall within a wide range from 50°C to 400°C. Thus liquid electrolytes may be used in the high temperature fuel cells, e.g. in through-flow or falling film configurations.

Above the phase transition, the ionic conductivity of the organic-inorganic hybrid compounds is between 1 and 40 mS/cm, i.e. at least $10^{-3}$ S/cm. As explained above, such a high conductivity allows for satisfactory performance of the compounds as a component of a proton conducting electrolyte such as a proton exchange membrane.

The conductivity through finite dimensions of a macroscopic nanocomposite membrane sample is subject to reaching the percolation threshold, which is approximately 67 % (salt content). At and above the threshold salt content the salt crystallites are in sufficiently close proximity to act as channels of ionic conductivity through the macroscopic sample, unless the other membrane components provide the suitable links for proton conduction. For example, the nanocomposite may self-assemble in such a way as to form proton-conductivity channels.

The organic-inorganic hybrid compounds prepared according to the described method having the general properties described above may be a liquid or a solid at room temperature and have suitable properties that allows it to act as the proton conducting component in blends or precursors that may be used to manufacture proton exchange membranes (PEM). The precursors contain one or more ion-conducting or non-conducting polymers or copolymers able to withstand on a long term basis the operating conditions of the electrochemical device in which they are applied and impart the membrane with properties conducive to the intended use of the membrane and its production. High-performance chemically resistant, organic polymers that may be fluorinated and may contain acidic or basic functional groups may be used in this function. Examples of polymers that may be used for the preparation of PEM include high-performance polymers such as polysulfone, polyethersulfone, polyphenylenesulfone, polyimide, polyimideamid, polyetherimide, polyetheretherketone, polyvinylidene fluoride and sulfonated derivatives thereof.

The polymer components of the PEM precursor composition may include a single polymer or copolymer, a mixture of two or more different polymers, a mixture of two or more different copolymers or a mixture of one or more polymers and one or more copolymers.

In the method of preparation of a PEM precursor composition according to the present invention, a salt solution is combined with a polymer solution in a compatible solvent. This ensures a homogeneous distribution of all components at molecular level and particularly of the salt in the polymer matrix. Known methods of membrane preparation which mix a salt into a polymer in solid form are unlikely to result in the fine distribution of nanoparticles needed to prepare a nanocomposite. The nanoparticles of organic-inorganic hybrid salt compound are formed within the polymer matrix of the membrane as the solvent evaporates from the membrane precursor composition. The solvent evaporation rate
influences the formation of nanoparticles, their size and distribution within the composite membrane. The solvent should be evaporated at a temperature below its boiling point.

Alternatively, the membrane may be prepared from a melt containing the polymer and salt, and the nanoparticles form within the polymer matrix as the melt cools and solidifies. For proton conducting membranes formed from a melt the mixture must be heated above the melting point of the polymers used, homogenized by means of mixing and cast through a suitable method such as calendering or similar.

In the method for preparing a proton exchange membrane precursor composition according to the present invention, the organic-inorganic hybrid salt which may be one of the salts 1 to 12 listed in the table above in combined with a polymer in the presence of a suitable compatible solvent. The solvent may be selected from the group consisting of dimethylformamide, dimethylacetamide, dimethylsulfoxide, N-ethylpyrrolidine and N-methyl-2-pyrroldione. The polymer may be selected from the group consisting of polysulfone, polyethersulfone, polyphenylenesulfone, polyimide, polylimideamide, polyetherimide, polyetheretherketone, polyvinylidene fluoride and derivatives thereof.

The one or more organic-inorganic hybrid compounds that may be used in the preparation of the conductor for protons may be synthesized in a separate reaction prior to use in forming the proton conducting composite material as described above or may be synthesized in-situ during the formation of the proton conducting composite material. The one or more organic-inorganic hybrid compounds contained in the composite proton conductive material may represent between 10 and 90 percent of the composite material dry weight. At below 10% weight content the conductivity of the membrane is poor and at above 90% the properties of the membrane such as flexibility, elasticity and elongation may be detrimentally affected.

The membranes prepared from the precursor composition of the present invention are nanocomposites. This is shown by the fact that the membranes, some of which contain more than 70 wt% of the salt are completely transparent. Membranes containing salt particles and crystals outside the nanoscale size range would not produce such transparent membranes.

Transparent membranes offer a number of advantages. The GDEs either side of the membrane in a MEA must be positioned precisely one above the other with the larger membrane between. Such positioning can be achieved manually, but can be achieved more easily and accurately by using optical positioning sensors in a positioning device. Transparent membranes facilitate this positioning.

Further support for the nanostructure of the salt particles within the membranes of the present invention is found in X-ray diffraction results (see Table 1 below). These show a reversible change in crystallinity during the phase transition with peaks for the nano-composite membranes matching peaks observed for the crystalline salt by itself. This implies that both samples contain the same type of
crystallites, however the transparency of the membranes proves that the membrane contains nano sizes crystals.

The precursor blend from which a proton conducting membrane may be manufactured may contain one or more inorganic fillers. As it is known to those skilled in the art, inorganic fillers may influence the mechanical and thermal stability of the PEM, modify the interaction of the membrane with water and influence transport properties. The one or more inorganic fillers that may be used in the preparation of blends from which membranes are manufactured may be added to the precursor composition in the form of nanometer and/or micrometer sized solids or they may be generated in situ during the manufacture of the PEM from the precursor composition. Inorganic fillers that may be used in the preparation of PEM may include one or more of silicon dioxide, aluminum oxide, titanium oxide, montmorillonite clays and derivatives thereof. Filler precursors that may be used to form inorganic fillers in situ during the formation of the membrane may be organic esters of orthosilicic acid.

Proton conducting membranes may be formed from a mixed material which is composed of one or more organic-inorganic hybrid compounds as described above, one or more polymers or copolymers, one or more inorganic fillers and low quantities, in the order of 0-4 wt% of processing aids such as surfactants.

Proper application of the described methods employing a solution or melt allows the formation of a homogeneous membrane with thicknesses between 10 and 500 µm. The organic-inorganic hybrid compound nanoparticles incorporated in the membrane are immobilized in the PEM structure through physical and/or chemical means which may include precipitation as an insoluble salt, entrapment in a matrix, non-covalent or covalent attachment to a component of the blend, and result in preventing leaching of the ion pair during use of the membrane.

PEMs manufactured through the methods of the present invention may be employed as proton conducting electrolytes in electrochemical devices. Such a membrane may be used in a fuel cell where it is placed between the anode and the cathode. The membrane electrode assembly (MEA) comprises the PEM and two gas diffusion electrodes (GDE), each placed on one side of the membrane in a manner that ensures sufficient contact and allows access for the fuel and oxidant to the catalyst. The manufacture of MEA with the PEM containing organic-inorganic hybrid compounds as described may involve the use of one or more of the following elements that enhance the properties of the MEA: pressure, heating and components of the mixture from which the PEM is formed or similar processes.

In general the MEA may be assembled by attaching both GDEs to the pre-formed PEM using a combination of appropriate conditions or bonding aids that result in a functional and physically stable assembly. Alternative methods of producing MEA may involve catalyst application on the cured or uncured membrane with subsequent GDE attachment. The membrane may also be formed during the
MEA manufacture by direct application of the mixed material in solution or melt form directly between two GDEs.

Fig. 13(a) depicts one embodiment of an MEA 20 according to the present invention. Fig. 13(b) shows the same MEA in an exploded view. MEA 20 consists of a proton conducting membrane 203 sandwiched between an upper gasket 202 and a lower gasket 205. An upper GDE 201 is placed against the upper gasket 202 and a lower GDE 204 is placed against the lower gasket 205. When assembled the MEA appears as depicted in Fig. 13(a).

Fig. 14 shows an exploded view of one embodiment of a fuel cell 30 according to the present invention which incorporates an MEA according to the present invention. An aluminium alloy end plate 301 includes gas connectors. Below the end plate lies a thermoelectric module 302. Below the thermoelectric module lies PTFE gaskets 303 and an electric insulator 304. An electric current collector 305 lies below the electric insulator. A graphite composite bipolar plate 306 is located below the current collector. The MEA 308 which consists of a proton conducting membrane sandwiched between two GDEs is held between two gaskets 307 and lies below the bipolar plate. The fuel cell 30 also includes an electric heater 309.

Fig. 15 is a photograph of certain embodiments of products according to the present invention. MEA 40 comprises proton conducting membrane 402 placed between two GDEs, of which only the upper GDE 401 is visible in the photograph. Separate membrane 402 and GDEs 401 are also shown to the bottom and left of the photograph.

The invention therefore provides high-temperature proton conducting electrolytes, proton exchange membranes, and membrane electrode assemblies containing polyoxometalate salts with organic cations, as well as the method for their manufacture and for the manufacture of the fuel cells employing them. The described compositions and devices are capable of proton conduction and operation without need for humidification at temperatures up to 300°C.

**Combinations**

It is appreciated that certain features of the invention, which are, for clarity, described in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention, which are, for brevity, described in the context of a single embodiment, may also be provided separately or in any suitable sub-combination.

The same is true for features described in the context of products and methods.

Any one or more of the aspects of the present invention may be combined with any one or more of the other aspects of the present invention. Similarly, any one or more of the features and optional features of any of the aspects may be applied to any one of the other aspects. Thus, the discussion
herein of optional and preferred features may apply to some or all of the aspects. Furthermore, optional and preferred features associated with a method or use may also apply to a product and vice versa. For example, optional and preferred features relating to the organic-inorganic hybrid compound, precursor composition, or nanocomposite proton-exchange membrane, methods of making the organic-inorganic hybrid compound, precursor composition, or nanocomposite proton-exchange membrane and methods of using the organic-inorganic hybrid compound, precursor composition, or nanocomposite proton-exchange membrane, etc apply to all of the other aspects. Furthermore, optional and preferred features associated with a method or use may also apply to a product (e.g. organic-inorganic hybrid compound, precursor composition, or nanocomposite proton-exchange membrane) and vice versa.

The options, features, preferences and so on mentioned herein apply both independently and in any combination, except where such a combination is expressly prohibited or clearly impermissible.

Examples

Polyoxometalate Salt Preparation

Example 1
A salt was synthesized by mixing aqueous solutions A and B. Solution A was obtained by dissolving 10 g of silicotungstic acid in 50 mL distilled water, solution B was obtained by dissolving 1.21 g of 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl]) and 1.71 g of 1,3-dimethylimidazol trifluoromethane sulfonate in 50 mL distilled water. The aqueous solution of ionic liquids was added into the aqueous solution of silicotungstic acid with automatic dosing pump (LAB PUMP Jr. Model RHSY, Fluid Metering Inc., Syosset, NY, USA) during 45 minutes mixing the solution. A white precipitate was formed. The suspension was mixed after the precipitation was completed for another 60 minutes. The precipitate was filtered and rinsed thoroughly with distilled water and then dried at 80°C in an oven overnight. 9.86 g of a crystalline solid was obtained which represents 90.07% of theoretical stoichiometric salt yield. The solid was characterized to have the composition SiWA-4(BMIM) + SiWA-4(DMIM). The obtained salt is soluble in N-methyl-2-pyrrolidone and imidazole mixture.

Example 1A
A salt was synthesized by mixing aqueous solutions A and B. Solution A was obtained by dissolving 10 g of phosphotungstic acid in 50 mL distilled water, solution B was obtained by dissolving 1.82 g of 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl]) in distilled water. Immediately upon mixing a white precipitate was formed. The precipitate was filtered and rinsed thoroughly with distilled water, and 9.55 g of a crystalline solid was obtained. The solid was characterized to have the composition PWA-3(BMIM), i.e. [BMIM]₃[PWi₂0₄o].

Example 1B
A series of salts was synthesized by carefully mixing aqueous solutions of silicotungstic acid (SiWA) and 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl]). Two aqueous solutions were prepared:
solution A containing SiWA in a concentration of around $7 \times 10^{-2}$ mol/L, and solution B containing BMIMCl of a concentration of around 0.3 mol/L. Solutions A and B were mixed in such a way as to combine SiWA and BMIMCl in molar ratios between $1:0.5$ and $1:7.5$. The obtained solid precipitate from each reaction was isolated, thoroughly rinsed, dried to constant mass at 105°C and weighed. The analysis showed as a plot in Fig 1 demonstrates that the precipitate formed has a stoichiometric ratio of one SiWA anion (i.e. [Wi2Si04o]4+) combined with exactly four BMIM cations regardless of the reagent ratio used.

**Example 2**

A salt was synthesized by mixing aqueous solutions A and B. Solution A was obtained by dissolving 10.63 g of phosphotungstic acid in 50 mL distilled water, solution B was obtained by dissolving 0.82 g of 1-butyl-3-methyl imidazolium chloride (BMIM)[Cl]) and 1.15 g of 1,3-dimethylimidazol trifluoromethane sulfonate in 50 mL distilled water. The aqueous solution of ionic liquids was added into the aqueous solution of silicotungstic acid with automatic dosing pump (LAB PUMP Jr. Model RHY, Fluid Metering Inc., Syosset, NY, USA) during 45 minutes mixing the solution. A white precipitate was formed. The suspension was mixed after the precipitation was completed for another 60 minutes. The precipitate was filtered and rinsed thoroughly with distilled water and then dried at 80°C in an oven overnight. 11.14 g of a crystalline solid was obtained which represents 93.0% of theoretical stoichiometric salt yield. The solid was characterized to have the composition PWA-3(BMIM) + PWA-3(DMIM). The obtained salt is soluble in N-methyl-2-pyrrolidone and imidazole mixture.

**Example 3**

A salt was synthesized by mixing aqueous solutions A and B. Solution A was obtained by dissolving 3.0 g of phosphotungstic acid (PWA) in 100 mL distilled water and solution B was obtained by dissolving 0.38 g of 1,2,3-trimethylimidazolium iodide ([TMIM][I]) in 110 mL distilled water. The aqueous solution of ionic liquids was slowly added to the aqueous solution of phosphotungstic acid during 60 minutes while continuously mixing the solution. A white precipitate was formed. After the addition was completed the suspension was mixed for another 120 minutes. The precipitate was filtered and rinsed thoroughly with distilled water and then dried at 80°C in an oven overnight. 2.90 g of a crystalline solid was obtained. The solid was characterized to have the composition PWA-3(TMIM). The obtained salt is soluble in an acetone/water mixture. Recrystallization of the salt from this solution gives monocrystals.

**Example 4**

A salt was synthesized by mixing aqueous solutions A and B. Solution A was obtained by dissolving 3.0 g of silicotungstic acid (SiWA) in 100 mL distilled water and solution B was obtained by dissolving 0.50 g of 1,2,3-trimethylimidazolium iodide ([TMIM][I]) in 110 mL distilled water. The aqueous solution of ionic liquids was slowly added to the aqueous solution of silicotungstic acid during 60 minutes while continuously mixing the solution. A white precipitate was formed. After the addition was completed
the suspension was mixed for another 120 minutes. The precipitate was filtered and rinsed thoroughly with distilled water and then dried at 80°C in an oven overnight. 1.62 g of a crystalline solid was obtained, which represents 81.0% of theoretical yield. The solid was characterized to have the composition SiWA-4(TMIM). The obtained salt is soluble in an acetonitrile/acetone/water mixture.

Example 5

A salt was synthesized by mixing aqueous solutions A and B. Solution A was obtained by dissolving 5 g of phosphotungstic acid in 25 mL distilled water and solution B was obtained by dissolving 1.71 g of 1,3-dimethyl imidazolium trifluoromethanesulfonate ([DMIMCF3SO3]) in 25 mL distilled water. The aqueous solution of ionic liquids was slowly added to the aqueous solution of phosphotungstic acid during 60 minutes while continuously mixing the solution. A white precipitate was formed. After the addition was completed the suspension was mixed for another 120 minutes. The precipitate was filtered and rinsed thoroughly with distilled water and then dried at 80°C in an oven overnight. 5.62 g of a crystalline solid was obtained which represents 96.07% of theoretical stoichiometric salt yield. The solid was characterized to have the composition PWA-3(DMIM). The obtained salt is soluble in N-Ethyl-2-pyrrolidone.

Example 6

A salt was synthesized by mixing aqueous solutions A and B. Solution A was obtained by dissolving 5 g of silicotungstic acid in 25 mL distilled water and solution B was obtained by dissolving 2.28 g of 1,3-dimethyl imidazolium trifluoromethanesulfonate ([DMIMCF3SO3]) in 25 mL distilled water. The aqueous solution of ionic liquids was slowly added to the aqueous solution of silicotungstic acid during 60 minutes while continuously mixing the solution. A white precipitate was formed. After the addition was completed the suspension was mixed for another 120 minutes. The precipitate was filtered and rinsed thoroughly with distilled water and then dried at 80°C in an oven overnight. 5.92 g of a crystalline solid was obtained which represents 96.4% of theoretical stoichiometric salt yield. The solid was characterized to have the composition SiWA-4(DMIM). The obtained salt is soluble in N-Ethyl-2-pyrrolidone (NEP).

Example 7

A salt was synthesized by mixing an aqueous solution of phosphotungstic acid and water-insoluble N-butyl-4-methylpyridinium hexafluorophosphate ([NBMP][PF6]). 3 g of phosphotungstic acid was dissolved in 50 mL of distilled water and 1.15 g of N-butyl-4-methylpyridinium hexafluorophosphate was added into solution during mixing. A white precipitate was formed. The suspension was mixed after the precipitation was completed for another 120 minutes. The precipitate was filtered and rinsed thoroughly with distilled water and then dried at 80°C in an oven overnight. 3.2 g of a crystalline solid was obtained which represents 90.14% of theoretical stoichiometric salt yield. The solid was characterized to have the composition PWA-3(NBMP). The obtained salt is soluble in acetonitrile and insoluble in water. Recrystallization of the salt in acetonitrile yields monocrystals. The structure and
elemental composition of the salt obtained with single crystal X-ray diffraction is given in Table 1 below and Figs 7a, 7b and Fig 8.

Table 1 - Single crystal X-ray structure determination of salt

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>K1529</th>
<th>(N-Bu-4-Me-Py)3PW12O40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assymmetric unit formula</td>
<td>C35H40N8O40P1W12</td>
<td></td>
</tr>
<tr>
<td>Assymmetric unit relative molecular mass</td>
<td>3327.87</td>
<td></td>
</tr>
<tr>
<td>Unit cell relative molecular mass</td>
<td>6655.74</td>
<td></td>
</tr>
<tr>
<td>Unit cell composition</td>
<td>C60H60N8O40P2W24</td>
<td></td>
</tr>
<tr>
<td>Unit cell parameters</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
  \[ \begin{align*} 
  a &= 11.7003(2) \text{ Å} \\
  b &= 12.5725(2) \text{ Å} \\
  c &= 22.6699(3) \text{ Å} \\
  \alpha &= 81.8275(11)^\circ \\
  \beta &= 75.5739(11)^\circ \\
  \gamma &= 69.2714(10)^\circ \\
  V &= 3015.21(8) \text{ Å}^3 
  \end{align*} \] |
| Crystal class and space group | triclinic, \(P - 1\) |
| Elemental composition of unit cell (wt.%) |  
  \[ \begin{align*} 
  10.83 \% & \text{ C,} \\
  1.45 \% & \text{ H,} \\
  1.26 \% & \text{ N,} \\
  19.23 \% & \text{ O,} \\
  0.93 \% & \text{ P,} \\
  66.29 \% & \text{ W} 
  \end{align*} \] |
| Cation mass fraction | 13.54 \% |

Example 8

A salt was synthesized by mixing an aqueous solution of silicotungstic acid and water-insoluble \(N\)-butyl-4-methylpyridinium hexafluorophosphate. 3.0 g of silicotungstic acid was dissolved in 50 mL of distilled water and 1.54 grams of \(N\)-butyl-4-methylpyridinium hexafluorophosphate ([NBMP][PF6]) was added into solution during mixing. A white precipitate was formed. The suspension was mixed after the precipitation was completed for another 120 minutes. The precipitate was filtered and rinsed thoroughly with distilled water and then dried at 80°C in an oven overnight. 3.30 g of a crystalline solid was obtained which represents 87.75% of theoretical stoichiometric salt yield. The solid was characterized to have the composition SiWA-4(NBMP). The obtained salt is soluble in acetonitrile and insoluble in water. Recrystallization of the salt in acetonitrile yields monocrystals.
Example 9
A salt was synthesized by mixing aqueous solutions A and B. Solution A was obtained by dissolving 5 g of silicotungstic acid in 25 mL distilled water and solution B was obtained by dissolving 1.35 g of 1-ethyl-3-methyl imidazolium methylsulfate ([EMIMCH3SO4]) in 25 mL distilled water. The aqueous solution of ionic liquids was slowly added to the aqueous solution of silicotungstic acid during 60 minutes while continuously mixing the solution. A white precipitate was formed. After the addition was completed the suspension was mixed for another 120 minutes. The precipitate was filtered and rinsed thoroughly with distilled water and then dried at 80°C in oven overnight. 4.93 g of a crystalline solid was obtained which represents 77.63% of theoretical stoichiometric salt yield. The solid was characterized to have the composition SiWA-4(EMIM). The obtained salt is soluble in dimethylformamide (DMF).

Example 10
A salt was synthesized by mixing an aqueous solution of 1.01 g phosphotungstic acid and 0.57 grams of trihexyltetradecylphosphonium chloride ([THTDP][Cl]) (molar ratio acid : IL = 1 : 3) in 7 mL of distilled water at room temperature. The solution was sonicated at 37 kHz and room temperature for 75 minutes. After that it was cooled to -5°C for 5 hours. The precipitate was then kept overnight at room temperature and then again sonicated at 80 kHz for 2 hours and cooled for 3 hours at -7°C. Finally, the precipitate was kept at room temperature overnight and rinsed with distilled water until the pH of water over the precipitate reached 5.5. The water was decanted and the precipitate dried at 80°C overnight and cooled to room temperature. 1.48 g of a white salt was obtained, which represents 99.3% of theoretical yield. The salt exhibits typical ionic liquid behaviour with a melting point below 85°C.

Example 11
A salt was synthesized by mixing an aqueous solution of 1.00 grams silicotungstic acid and 0.73 grams of trihexyltetradecylphosphonium chloride ([THTDP][Cl]) (molar ratio acid : IL = 1 : 4) in 7 mL of distilled water at room temperature. The solution was sonicated at 37 kHz and room temperature for 75 minutes. After that it was cooled to -5°C for 5 hours. The precipitate was kept overnight at room temperature and then again sonicated at 80 kHz for 2 hours and cooled for 3 hours at -7°C. Finally, the precipitate was kept at room temperature overnight and rinsed with distilled water until the pH of water over the precipitate reached 5.5. The water was decanted and the precipitate dried at 80°C overnight and cooled to room temperature. 1.28 g of a white salt was obtained, which represents 99.6% of theoretical yield. The salt exhibited typical ionic liquid behavior with a melting point below 60 °C.

Example 12
A salt was synthesized by mixing aqueous solution of 1.00 g phosphotungstic acid and 0.80 g of trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl) amide ([THTDPKNS2O4C2F6]) (molar ratio acid : IL = 1 : 3) in 7 mL of distilled water at room temperature. The solution was sonicated at 37 kHz and room temperature for 75 minutes. After that it was cooled to -5°C for 5 hours. The precipitate
was then kept overnight at room temperature and then again sonicated at 80 kHz for 2 hours and cooled for 3 hours at -7°C. Finally, the precipitate was kept at room temperature overnight and rinsed with distilled water until the pH of water over the precipitate reached 5.5. The water was decanted and the precipitate dried at 80°C overnight and cooled to room temperature. 1.44 g of a pale yellow salt was obtained, which represents 90.2% of theoretical yield. This salt exhibits typical ionic liquid behaviour with a melting point below 75°C.

Example 13
A salt was synthesized by mixing aqueous solutions A and B. Solution A was obtained by dissolving 3 g of silicotungstic acid in 60 mL distilled water and solution B was obtained by dissolving 1.5 g of polyimidazolium bromide (PIB) in 30 mL distilled water. The aqueous solution of ionic liquid was slowly added to the aqueous solution of silicotungstic acid during 60 minutes while continuously mixing the solution. A white precipitate was formed. After the addition was completed the suspension was mixed for another 120 minutes. The precipitate was filtered and rinsed thoroughly with distilled water and then dried at 80°C in an oven overnight. 4.3 g of a crystalline solid was obtained which represents 95.56% of theoretical stoichiometric salt yield. The solid was characterized to have the composition SiWA-4(PIB). The obtained salt is soluble in low concentrations in N-methyl-2-pyrrolidone (NMP).

Composite Membrane Preparation

Example 14
A nanocomposite membrane was prepared by dissolving 1.0 g of polyamideimide (PAI) and 1.0 g of sulfonated polyetheretherketone (SPEEK) in 8 mL of N-methyl-2-pyrrolidone by stirring the solution at 80°C for 120 minutes until a clear solution was obtained. Then 1.4 g of the salt described in Example 1 and 0.4 g of imidazole (to enhance the intermolecular proton transfer, as explained above) were dissolved by stirring the solution at 80°C for another 90 minutes. The temperature of the solution was increased to 100°C and the solution was stirred for 20 minutes. Again, the temperature of the solution was increased to 120°C and the solution was stirred for another 10 minutes to obtain a clear light brown solution. The solution was cast on glass substrate put on applicator with 500 µm knife at linear velocity of 1 mm/sec. The obtained film was dried at 150°C in a laboratory dryer for 12 hours. After cooling the glass plate to room temperature the obtained membrane was rinsed with distilled water and detached from the glass plate. The obtained membrane was pale yellow, transparent and smooth with a thickness of 70 µm.

Example 14A
A solution suitable for casting proton conducting membranes was prepared by mixing solutions A and B. Solution A was a 27 w/w % of polyimide P84 in dimethylformamide, solution B was prepared by dissolving 0.6 g of an organic-inorganic ion pair prepared by reaction between phosphotungstic acid (PWA) and 1-butyl-3-methyl imidazolium hexafluorophosphate ([BMMHPFe]) in 2 mL of dimethylformamide. Solution B was then slowly added to 3.50 g of solution A and the solution was
mixed in such a manner as to yield a homogeneous, viscous, yellowish solution without air bubbles. The solution was cast by means of a blade applicator on a glass plate. After drying to remove the solvent a 90 µm thick homogeneous film was removed from the glass plate.

Example 15
A nanocomposite membrane was prepared by dissolving 0.9 g of the salt described in Example 2, 1.01 g of polyamideimide (PAI) and 0.36 g of E6020 P (25% in dimethylformamide) in a mixture of 3.5 mL of N-methyl-2-pyrrolidone and 0.05 g of water (MiliQ) (the small amount of water was added to control the surface tension needed for film formation) by stirring the solution at 180°C for 150 minutes until a clear solution was obtained. The solution was then cooled to 120°C and left to stay at that temperature for 15 minutes. The solution was then cast on applicator with 300 µm hot knife at linear velocity of 0.5 mm/sec on glass substrate. The obtained film was dried at 150°C in a laboratory dryer for 2 hours. The obtained membrane was light yellow, transparent and smooth with a thickness of 80 µm.

Membrane-Electrode Assembly Preparation and Single Cell Tests
Example 16
Two commercial electrodes (FuelCellsEtc) with Pt loading 0.5 mg/cm² cut to 5 x 5 cm² dimension were used for membrane-electrode assembly preparation. The catalyst layer of each electrode was brushed with 100 µL of a solution of salt synthesized according to Example 1 in a mixture of N-methyl-2-pyrrolidone and imidazole. To prepare such a solution 0.1 g of SiWA-4(BMIM) + SiWA-4(DMIM) salt mixture was dissolved in a mixture of 0.2 mL of N-methyl-2-pyrrolidone and 0.03 g of imidazole. The electrodes were then dried in laboratory drier for 15 minutes at 120°C. The membrane prepared according to Example 14 was cut to 6.5 x 6.5 cm² dimension and put between the electrodes. The membrane-electrode assembly was then formed in a heated vacuum press at 135°C, 30 bar for 5 minutes. The obtained MEA was tested in a single cell test station (Baltic FuelCell qCf FC25/1 00 v 1.1) at 195°C, 20 ml/min flow of dry hydrogen on anode side, 20 ml/min flow of dry oxygen on cathode side. The cell was pressed at two different pressures: 1 bar and 2 bar. The obtained polarization curves are presented in Fig 9.

Example 16A
A cured PEM containing a polyamideimide and a 1-butyl-3-methyl imidazolium cation-silicotungstate anion ion pair was bonded to standard high temperature fuel cell electrodes following the process:
The membrane and electrodes were cut to size. The membrane was cut as a 5.5 x 5.5 cm square, and the electrodes as 4.5 x 4.5 cm squares. The electrodes were lightly moistened on the catalyst side using a diluted N-methyl pyrrolidine solution that was used to cast the membrane. The membrane electrode assembly was then put together with one electrode on either side of the membrane, with the moistened catalyst side facing the membrane. The MEA was then pressed with 10 kg and placed in a drying oven heated to 160°C. After 4 hours the finished MEA was removed.
Example 16B
A cured PEM was bonded to standard high temperature fuel cell gas diffusion electrodes following the process: The membrane and electrodes were cut to size. The membrane was cut as a 6.5 x 6.5 cm square, and the electrodes as 5.0 x 5.0 cm squares. The electrodes were lightly moistened on the catalyst side using a diluted N-methyl pyrrolidine solution that was used to cast the membrane. The membrane electrode assembly was then put together with one electrode on either side of the membrane, with the moistened catalyst side facing the membrane. The MEA was then pressed with 4 kg and cured in an oven at 150°C. After 2 hours the temperature was raised to 200°C and the curing was continued for 1 hour. The MEA was allowed to slowly cool to room temperature after which it was ready for use.

Example 16C
A MEA was prepared, composed of Pt/C gas diffusion electrodes (FuelCellsEtc) and a 100 µιη proton exchange membrane made from N-methylpyrrolidone solution of a polyimideamide and sulfonated polyetheretherketone (1:1) mixture with a salt prepared from [BMIM][Cl] and DMIMTf (in mixture of 1:1 molar ratio) and SiWA. The salt content in the membrane was 40 wt%. The MEA was placed into a test single cell and the polarization curves were measured. The polarization and power curves shown in Fig 6 were recovered at 195°C with dry oxygen feed (20 ml/min) and at 250°C with air feed (self-breathing, open parallel channels) at cathode side, and a dry hydrogen feed (20 ml/min) at anode side.

Example 17
Two commercial electrodes (FuelCellsEtc) with Pt loading 0.5 mg/cm² cut to 5 x 5 cm² dimension were used for membrane-electrode assembly preparation. A solution 0.20 g of salt synthesized in Example 2 was dissolved in 0.30 mL of N-methyl-2-pyrrolidone and the solution was heated at 150°C for 10 minutes. The catalyst layer of each electrode was brushed with 100 µL of a hot solution. The membrane prepared according to Example 15 was cut to 6.5 x 6.5 cm² dimension and put between the wet electrodes. The membrane-electrode assembly was then formed in a heated vacuum press at 135°C, 50 bar for 2.5 minutes. The obtained MEA was tested in a single cell test station (Baltic FuelCell qCf FC25/1 00 v 1.1) at 195°C, 20 ml/min flow of dry hydrogen on anode side, 20 ml/min flow of dry oxygen on cathode side. The cell was pressed at 1 bar pressure. The obtained polarization curve is presented in Fig 10.

Example 18
Two electrodes with with proprietary Pt-skin over ordered PtCu3 alloyed nanoparticles supported on graphitized carbon inkjet printed on carbon cloth with Pt loading 0.2 mg/cm² cut to 5 x 5 cm² dimension were used for membrane-electrode assembly preparation. A solution 0.14 g of salt prepared in Example 1 was dissolved in mixture of 0.20 mL of N-methyl-2-pyrrolidone and 0.04 g of imidazole and the solution was brushed on the catalyst layer of both electrodes. The electrodes were dried at 100°C for 15 minutes. The membrane prepared according to Example 14 was cut to 6.5 x 6.5
cm² dimension and put between the electrodes. The membrane-electrode assembly was then formed in a laboratory hot vacuum press at 135°C, 44 bar for 4.5 minutes. The obtained MEA was tested in a single cell test station (Baltic FuelCell qCl FC25/100 v1.1) at 195°C with 20 ml/min flow of dry hydrogen on anode side and 20 ml/min flow of dry oxygen on cathode side. The cell was pressed at 1 bar. The obtained polarization curve is presented in Fig 11.

Example 19

Two electrodes with with proprietary Pt-skin over ordered PtCu3 alloyed nanoparticles supported on graphitized carbon inkjet printed on carbon paper with Pt loading 0.14 mg/cm² cut to 3.4 x 3.4 cm² dimension were used for membrane-electrode assembly preparation. A solution 0.14 g of salt prepared in Example 1 was dissolved in mixture of 0.20 mL of N-methyl-2-pyrrolidone and 0.04 g of imidazole and the solution was brushed on the catalyst layer of both electrodes. The electrodes were dried at 100°C for 15 minutes. The membrane prepared according to Example 14 was cut to 4.5 x 4.5 cm² dimension and put between the electrodes. The membrane-electrode assembly was then formed in a laboratory hot vacuum press at 135°C, 30 bar for 2 minutes. The obtained MEA was tested in a proprietary single cell at 245°C with 20 ml/min flow of dry hydrogen on anode side and 20 ml/min flow of ambient air on cathode side. The obtained polarization curve is presented in Fig 12.

Example 20

An ion pair was produced by the method according to the present invention and had a stoichiometric composition where the combined charge of the organic cations matches exactly the charge of the polyoxometalate anion. A detailed and systematic quantitative study of the ion pairs produced by this method showed that regardless of excess of one reagent a single, stoichiometric cation vs. anion ratio is formed for a given organic cation - polyoxometalate anion ion pair. Fig 1 demonstrates one example showing the mass balance of the ion exchange reaction between silicotungstic acid and an imidazolium chloride ionic liquid at different reagent ratios.

Example 21

A purified organic cation - polyoxometalate anion ion pair according to the present invention was prepared in the form of a single crystal. X-ray diffraction analysis of the structures confirmed an exact stoichiometric composition of the ion pair. Fig 2 shows one example of the single crystal structure of an ion pair formed by the reaction of phosphotungstic acid hydrate and 1-butyl-3-methyl imidazolium hexafluorophosphate (BMIMPFe).

Example 22

The ion pairs prepared by the method according to the present invention are insoluble in water and are highly stable. They may be in the form of liquids or solids. The ion pairs are not hygroscopic. Thermal gravimetric analysis has revealed that the said ion pairs prepared by the methods outlined in this disclosure have high thermal stability with a minor loss of weight up to temperatures 300°C or more. Fig 3 shows a thermogram giving a representative illustration of said characteristics. The
described thermal behavior also shows that the ion pair, made by reacting silicotungstic acid and BMIMCI, is not in hydrated form at ambient conditions, indicating that the transition from a heteropolyacid to an organic cation-polyoxometalate anion ion pair radically alters the affinity of the material towards water.

Example 23

Impedance spectroscopy measurements were used to investigate the special ionic conductivity properties of the ion pairs according to the present invention which are intrinsically linked to their chemical structure, and have shown that the ion pair exhibits low ionic conductivity up to the order 10⁻⁴ S/cm up to a temperature where a phase transition occurs. This transition coincides with a rapid increase in ionic conductivity by several orders of magnitude. Further heating above the transition temperature causes the ionic conductivity to increase further albeit at a much lower rate. Upon cooling the ionic conductivity is reduced in a reversible way although the conductivity transition cycle may exhibit a hysteresis, with the cooling phase transition occurring at a temperature lower than the temperature of the phase transition during heating.

Fig 4 shows a representative conductivity vs. reciprocal temperature diagram obtained from impedance spectroscopy measurement in dry helium of an ion pair prepared by the reaction of silicotungstic acid with BMIMCI and exhibiting the above-described dependence of ionic conductivity on reciprocal temperature, including the hysteresis effect. The example shows that the phase transition occurs at 182°C, where an increase in the ionic conductivity by approximately three orders of magnitude takes place. A high ionic conductivity on the order of 10⁻² S/cm was achieved at temperatures up to 299°C. Upon cooling the phase transition temperature is 140°C. This example illustrates that the organic cation-polyoxometalate anion ion pair is capable of sustaining ionic conductivity above 10⁻² S/cm in the temperature range 195-300°C without the presence of water.

Example 24

The phase transition at which the ionic conductivity of the ion pair formed by the reaction of silicotungstic acid and BMIMCI containing a polyoxometalate anion undergoes a significant change in ionic conductivity coincides with a thermal absorption peak that can be detected by differential scanning calorimetry (DSC). A representative DSC thermogram is shown in Fig 5. An endothermic peak occurs at 190.6°C in the heating scan, which corresponds exactly with the ionic conductivity jump observed by impedance spectroscopy. The exothermic peak in the cooling scan occurs at 132.3°C. Heat flows for the endothermic and exothermic peaks are equal in magnitude confirming that this is a reversible transition. Consecutive heating scans show that the transition is repeatable.

The peaks observed in the DSC thermograms resemble a thermogram trace resulting from melting however inspection of a sample on a melting point apparatus during heating revealed that melting does not occur at the temperature where the transition takes place as observed by the thermal
analytical methods listed above. These results indicate that the described ionic pairs undergo an order-disorder phase transition.

Example 25

Fig 6 illustrates that a fuel cell employing the described proton conducting membrane is capable of sustained operation at temperatures between 195 and 300°C without any humidification of reactant gases by which it may be distinguished from other fuel cells employing polymer based proton exchange membranes. It shows two pairs of polarization and power curves: one measured at 250°C in a 12 cm² single cell on a MEA manufactured through the methods described in this disclosure, Example 16C, employing dry hydrogen and ambient air as fuel and oxidant, respectively, and the other measured at 195°C in a 25 cm² single cell on the MEA with the same composition but employing dry hydrogen and oxygen as fuel and oxidant, respectively.
Claims

1. An organic-inorganic hybrid compound comprising a salt of an organic cation with a polyoxometalate anion, comprising a stoichiometric ratio of organic cation to polyoxometalate anion.

2. An organic-inorganic hybrid compound according to claim 1, wherein the organic cation is defined according to any one of the following formulae:

\[
\begin{align*}
(I) & \quad \text{R}^1 \quad \text{R}^2 \quad \text{R}^3 \\
(II) & \quad \text{R}^4 \quad \text{R}^5 \\
(III) & \quad \text{R}^6 \quad \text{R}^7 \quad \text{R}^8 \quad \text{R}^9 \\
(IV) & \quad \text{R}^{10} \\
\end{align*}
\]

wherein

- \( \text{R}^1 \) and \( \text{R}^2 \) are each independently saturated aliphatic \( \text{d}^n\text{alkyl} \);
- \( \text{R}^3 \) is independently hydrogen, or linear or branched \( \text{Ci-4alkyl} \);
- \( \text{R}^4 \) and \( \text{R}^5 \) are each independently saturated aliphatic \( \text{d}^n\text{alkyl} \);
- \( \text{R}^6, \text{R}^7, \text{R}^8 \) and \( \text{R}^9 \) are each independently selected from linear or branched \( \text{Cs}-\text{isalkyl} \);
- \( \text{R}^{10} \) is independently selected from a linker group comprising a group independently selected from aryl, heteroaryl, cycloaliphatic, alkenyl and alkynyl; and
- \( n \) is an integer within the range from 5 to 1000;

wherein the organic cation is optionally not 1-butyl-3-methylimidazolium.

3. An organic-inorganic hybrid compound according to claim 1 or 2, wherein the organic cation is selected from DMIM, EMIM, TMIM, NBMP, THTDP and PIM.
4. An organic-inorganic hybrid compound according to any one of the preceding claims, wherein the polyoxometalate anion is an isopolyoxometalate or a heteropolyoxometalate comprising a transition metal atom selected from W, V, Mo, Nb, Mn and Ce.

5. An organic-inorganic hybrid compound according to any one of the preceding claims, wherein the polyoxometalate anion is selected from silicotungstate and phosphotungstate.

6. A method of making an organic-inorganic hybrid compound comprising the steps of, mixing a heteropolyacid with an organic salt comprising an organic cation and a counter anion, wherein the organic-inorganic hybrid compound formed comprises a stoichiometric ratio of organic cation to polyoxometalate anion.

7. A method according to claim 6, wherein the reaction product is washed with a washing solvent in which the organic-inorganic hybrid compound is insoluble, but in which other species present in the reaction mixture are soluble.

8. A method according to claim 7, wherein the washing solvent is water.

9. A method according to any one of claims 6 to 8, wherein the further step of recrystallization of the organic-inorganic hybrid compound is performed.

10. A method according to any one of claims 6 to 9, wherein the organic cation is selected from DMIM, EMIM, TMIM, NBMP, THTDP and PIM.

11. A method according to any one of claims 6 to 10, wherein the counter anion in the organic salt is chloride, bromide, iodide, tetrafluoroborate, hexafluorophosphate, trifluoroacetate, methylsulfate, trifluoromethanesulfonate or trifluoromethanesulfonimide.

12. A method according to any one of claims 6 to 11, wherein the organic salt is insoluble in water.

13. An organic-inorganic hybrid compound produced by a method according to any one of claims 5 to 7.

14. A precursor composition comprising
   a polymer component;
   an organic salt comprising
   a polyoxometalate anion and an organic cation, or
   an organic-inorganic hybrid compound according to any one of claims 1 to 5; and
   a compatible solvent.
15. A precursor composition according to claim 14, wherein the organic cation is selected from DMIM, EMIM, TMIM, NBMP, THTDP and PIM.

16. A precursor composition according to claim 14 or 15, wherein the polymer component comprises a polymer selected from polysulfone, polyethersulfone, polyphenylenesulfone, polyimide, polyimideamide, polyetherimide, polyetheretherketone, polyvinylidene fluoride and derivatives thereof.

17. A precursor composition according to any one of claims 14 to 16, wherein the compatible solvent comprises a solvent selected from dimethylformamide, dimethylacetamide, dimethylsulfoxide, N-ethylpyrrolidine and N-methyl-2-pyrrolidone.

18. A method of making a precursor composition, comprising the steps of,
   combining a polymer component with a proton conducting component in the presence of a compatible solvent;
   wherein the proton conducting component is an organic salt comprising
   an organic cation and a polyoxometalate anion, or
   an organic-inorganic hybrid compound according to any one of claims 1 to 5; and
   mixing to produce a homogeneous composition.

19. A method according to claim 18, wherein the organic cation is selected from DMIM, EMIM, TMIM, NBMP, THTDP and PIM.

20. A method according to claim 18 or 19, wherein the proton conducting component is synthesized in situ in the presence of the polymer.

21. A method according to any one of claims 18 to 20, wherein the polymer component comprises a polymer selected from polysulfone, polyethersulfone, polyphenylenesulfone, polyimide, polyimideamide, polyetherimide, polyetheretherketone, polyvinylidene fluoride and derivatives thereof.

22. A method according to any one of claims 18 to 21, wherein the compatible solvent comprises a solvent selected from dimethylformamide, dimethylacetamide, dimethylsulfoxide, N-ethylpyrrolidine and N-methyl-2-pyrrolidone.

23. A precursor composition made by the method according to any one of claims 18 to 22.

24. A nanocomposite proton-exchange membrane, comprising
   a polymer matrix comprising a polymer; and
   polyoxometalate nanoparticles embedded within the polymer matrix, the nanoparticles comprising
   an organic cation and a polyoxometalate anion, or
an organic-inorganic hybrid compound according to any one of claims 1 to 5.

25. A nanocomposite proton-exchange membrane according to claim 24, wherein the nanoparticles are homogeneously dispersed through the membrane.

26. A nanocomposite proton-exchange membrane according to claim 24 or 25, wherein the organic cation is selected from DMIM, EMIM, TMIM, NBMP, THTDP and PIM.

27. A nanocomposite proton-exchange membrane according to any one of claims 24 to 26, wherein the polyoxometalate nanoparticles make up between 10 and 90 wt% of the total dry membrane weight.

28. A nanocomposite proton-exchange membrane according to any one of claims 24 to 27, wherein the polymer is selected from polysulfone, polyethersulfone, polyphenylenesulfone, polyimide, polyimideamide, polyetherimide, polyetheretherketone, polyvinylidene fluoride and derivatives thereof.

29. A method of making a nanocomposite proton-exchange membrane, comprising the steps of, applying the precursor composition according to any one of claims 14 to 17, or a precursor composition made by the method according to any one of claims 18 to 22, to a surface, or applying a melt comprising the organic-inorganic hybrid compound according to any one of claims 1 to 5 and a polymer to a substrate; and optionally drying to produce a membrane.

30. A method according to claim 29, wherein the precursor composition or melt is applied to the surface by blade application, dip coating or spin coating.

31. A method according to claim 29 or 30, wherein the polymer is selected from polysulfone, polyethersulfone, polyphenylenesulfone, polyimide, polyimideamide, polyetherimide, polyetheretherketone, polyvinylidene fluoride and derivatives thereof.

32. A nanocomposite proton-exchange membrane made by the method according to any one of claims 29 to 31.

33. A membrane-electrode assembly comprising; a nanocomposite proton-exchange membrane according to any one of claims 24 to 28, or a nanocomposite proton-exchange membrane made by a method according to any one of claims 29 to 31, between two gas diffusion electrodes.

34. A method of making a membrane-electrode assembly comprising the steps of,
attaching a first gas diffusion electrode to a first surface and a second gas diffusion electrode to a second surface of the membrane according to any one of claims 24 to 28, or a membrane made by a method according to any one of claims 29 to 31.

35. A method according to claim 34, wherein a precursor composition according to any one of claims 14 to 17, or a precursor composition made by a method according to any one of claims 18 to 22, is applied to an inner surface of the first gas diffusion electrode and/or the second gas diffusion electrode before attachment to the membrane.

36. A method according to claim 34 or 35, wherein one or more of heat and pressure is applied during attachment of the gas diffusion electrodes.

37. A method of making a membrane-electrode assembly comprising the steps of,
applying a precursor composition according to any one of claims 14 to 17, or a composition made by a method according to any one of claims 18 to 22, to the inner surface of a first gas diffusion electrode; and
attaching a second gas diffusion electrode to the applied composition.

38. A method of making a membrane-electrode assembly according to claim 37, comprising the step of drying the applied precursor composition before attachment of the second gas diffusion electrode.

39. A membrane-electrode assembly made by a method according to any one of claims 34 to 38.

40. A fuel cell comprising the membrane-electrode assembly according to claim 33, or a membrane electrode assembly made by a method according to any one of claims 34 to 38.

41. Use of a nanocomposite proton-exchange membrane according to any one of claims 24 to 28, or a membrane made by a method according to any one of claims 29 to 31, as a proton-conducting electrolyte in a fuel cell.

42. A fuel cell substantially as described herein with reference to, and as illustrated in, the accompanying drawings.

43. A membrane-electrode assembly substantially as described herein with reference to, and as illustrated in, the accompanying drawings.

44. A nanocomposite proton-exchange membrane substantially as described herein with reference to, and as illustrated in, the accompanying drawings.
Figure 1
Figure 4
Figure 5
Figure 6
Figure 9
Pol 1 P = 1 bar

Figure 11
Figure 12
INTERNATIONAL SEARCH REPORT

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. □ Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. [X] claims Nos. 1-13 (partially) because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

   see FURTHER INFORMATION sheet PCT/ISA/210

3. □ Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 64(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. □ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. □ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of additional fees.

3. □ As only some of the required additional search fees were timely paid by the applicant, this international search report covers 0% of the invention. Search results for these claims Nos.:

4. [X] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

   1-13

Remark on Protest

□ The additional search fees were accompanied by the applicant’s protest and, where applicable, the payment of a protest fee.

□ The additional search fees were accompanied by the applicant’s protest but the applicable protest fee was not paid within the time limit specified in the invitation.

□ No protest accompanied the payment of additional search fees.

Form PCT/ISA/21 0 (continuation of first sheet (2)) (April 2005)
**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/EP2014/07Q697

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C07F11/00  B01J23/00  B01J23/89  H01M8/10

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

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C07F  B01J  H01M

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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</thead>
<tbody>
<tr>
<td>X</td>
<td>WO 2006/080766 AI (UNIV INDUSTRY UNIVERSITY C00PE [KR]; LEE YOUNG-MOON [KR]; LEE CHANG-HYUN) 3 August 2006 (2006-08-03) An acido doped proton conducting polymer, wherein the acid is chosen of 1-Methyl-3-methyl imidazolium cation (BMIM), which is doped with a proton-conducting inorganic filler from the group comprising phosphotungstic acid (PWA), phosphomolybdenic acid, silicotungstic acid (SiWA), molybdophosphoric acid, silicomolybdenic acid: claims 3 and 8 both being dependent on claim 2; claims 40 and 47 both being dependent on claim 37; Use of such acid-doped proton conducting polymers for polymer membranes in fuel cells: Page 1, lines 1-4</td>
<td>1-13</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C.  See patent family annex.

* Special categories of cited documents:
  - "A" document defining the general state of the art which is not considered to be of particular relevance
  - "E" earlier application or patent but published on or after the international filing date
  - "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  - "O" document relating to an oral disclosure, use, exhibition or other means
  - "P" document published prior to the international filing date but later than the priority date claimed
  - "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  - "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  - "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
  - "A" document member of the same patent family

**Date of the actual completion of the international search**

19 June 2015

**Date of mailing of the international search report**

17/09/2015

**Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk**

Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

**Authorized officer**

Lange, Tim
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<tr>
<td>X</td>
<td><strong>CN 103 665 369 A</strong> (LANZHOU CHEM PHYS INST) 26 March 2014 (2014-03-26) Polyethyl ene glycol-functional polyoxometalate ion liquid obtained by ion exchange reaction between the polyethyl ene glycol imidazolium chloride dodecopolymer and the polyoxometalate ion acid obtained in the polyethylene glycol functional polyoxometalate ion liquid. Hybrid compound of organic cation and inorganic anion: Formulae page 6/bottom to page 17 top. Use of these organic-inorganic hybrid compounds in field where high specific conductivity is needed such as in fuel cells.</td>
<td>1.6, 13</td>
</tr>
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<td>X</td>
<td><strong>CN 103 666 536 A</strong> (UNIV LIAO NING PET CHEM TECH) 26 March 2014 (2014-03-26) The compounds of claim 2, page 2 Use of the compounds as FCC gasoline desulfurization catalysts</td>
<td>1-8, 10-13</td>
</tr>
<tr>
<td>X</td>
<td><strong>US 2013/085191 A1</strong> (LASKOSKI MATTHEW [US]) 4 April 2013 (2013-04-04) Examples 3, 10, 16 Use as catalysts for the destruction of chemical warfare agents</td>
<td>1.6, 13</td>
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<td>Category</td>
<td>Citation of document, with indication, where appropriate, of the relevant passages</td>
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<td>X</td>
<td>CN 103 333 114 A (UNIV QINGDAO SCIENCE &amp; TECHNOLOGY) 2 October 2013 (2013-10-02) Imidazolium and pyridinium um-based salts of polyoxometalates: Compounds 1-6 Use as ionic liquids -----.</td>
<td>1-8, 10-13</td>
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<td>X</td>
<td>CN 101 219 995 A (UNIV EAST CHINA SCIENCE &amp; TECHNOLOGY [CN]) 16 July 2008 (2008-07-16) Organoc-iminocarbamate materials with the organo cations on page 3, bottom and the heteropolyoxometalates of page 4, The PEGylated imidazolium salts on pages 6-13 Use as ionic liquids -----.</td>
<td>1-6, 13</td>
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<td>X</td>
<td>WO 2009/108222 A2 (3M INNOVATIVE PROPERTIES CO [US] ; COLORADO SCHOOL OF MINES [US]) 3 September 2009 (2009-09-03) Bi s(methacryl si lyl) dodeca-tungsi sti cate TMA [(CH3)4] [al pha-SiW11039]0 [Si (CH2)3C(0) CCH3CH2]2 Bi s(methacryl si lyl) dodeca-tungsi sti cate TMA sal t [(CH3)4] [(si)2] [(C4H9)4] [gamma-SiW10036]0 [Si (CH2)3C(0) CCCH3CH2]2 Bi s(methacryl si lyl) dodeca-tungsi sti cate TMA sal t [(CH3)4] [(si)2] [(C4H9)4] [gamma-SiW10036]0 [Si (CH2)3C(0) CCCH3CH2]2 and others as disclosed in Table 2, page 18 A composition comprising a polymer component, a polyoxometalate and a counter ion to the polyoxometalate: claim 1 and Table 3 A fuel cell polymer electrolyte membrane: claim 5 -----</td>
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<td>X</td>
<td>CN 103 288 739 A (UNIV SHAANXI NORMAL) 11 September 2013 (2013-09-11) A complex of heteropolytungstate acid anions and alkyl imidazolium cations represented by [MMI] [EMI] b [PMI] c [BMIj] d [XW12040] n. [MMI], [EMI], [PMI] and [BMI] respectively represent 1-methyl -3-methyl imidazolium cations, 1-ethyl -3-methyl imidazolium cations, 1-propyl -3-methyl imidazolium cations, and 1-butyl -3-methyl imidazolium cations.</td>
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<td>T</td>
<td>US 6 059 943 A (MURPHY OLIVER J [US] ET AL) 9 May 2000 (2000-05-09) Composite membrane with inorganic oxide cation exchange particles as proton-conductor (claims 5, 18), the polyoxometalates being heteropolytungstate or heteropolymolybdates (claim 29) Use as conducting membranes for fuel cells (column 1, lines 13-14) -----</td>
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<td>Publication date</td>
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<td>US 6387230 B1 14-05-2002</td>
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FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-13

Organic-inorganic hybrid compound comprising an organic cation and a polyoxometalate anion. Methods of making this hybrid compound and the hybrid compound made by this method.

2. claims: 14-23

Precursor composition of comprising a polymer component, an organic salt comprising a polyoxometalate anion and organic cation and a compatible solvent. Methods of making this precursor and the Precursor composition made by this method.

3. claims: 24-32, 41, 44

Nanocomposite proton-exchange membrane comprising a polymer matrix, a polyoxometalate nanoparticle comprising an organic cation and a polyoxometalate anion, methods of making this membrane and the Nanocomposite proton-exchange membrane made by the method.

4. claims: 33-39, 43

Membrane electrode assembly comprising a nanocomposite proton-exchange membrane that comprises polyoxometalate nanoparticles in a polymer matrix; Methods of making such a membrane-electrode assembly and the membrane-electrode assembly made by this method.

5. claims: 40, 42

Fuel cell comprising the membrane electrode assembly that comprises a nanocomposite proton-exchange membrane containing polyoxometalate nanoparticles.
Continuation of Box 11.2

Claims Nos.: 1-13 (partially)

The initial phase of the search revealed a very large number of documents relevant to the issue of novelty. So many documents were retrieved that it is impossible to determine which parts of claims 1-13 may be said to define subject-matter for which protection might legitimately be sought (Article 6 PCT). For these reasons, the search was performed taking into consideration the non-compliance in determining the extent of the search of claims 1-13.

The search of claims 1-13 was restricted to the actual examples of hybrid material as disclosed in examples 1-13. Only in this respect is the search report complete.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examination Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the applicant proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.