Compounds for novel proton conducting membranes and methods of making same

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Abstract
The present invention provides new compounds for use in proton exchanging membranes which are able to operate in a wide variety of temperature ranges, including in the intermediate temperature range of about 100°C. to 700°C., and new and improved methods of making these compounds. The present invention also provides new and improved methods for making chalcogenide compounds, including, but not limited to, non-protonated sulfide, selenide and telluride compounds. In one embodiment, the proton conductivity of the compounds is between about $10^{-8}$ S/cm and $10^{-1}$ S/cm within a temperature range of between about −50 and 500°C.

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COMPOUNDS FOR NOVEL PROTON CONDUCTING MEMBRANES AND METHODS OF MAKING SAME

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See application file for complete search history.

References Cited
U.S. PATENT DOCUMENTS

FOREIGN PATENT DOCUMENTS

OTHER PUBLICATIONS


ABSTRACT
The present invention provides new compounds for use in proton exchange membranes which are able to operate in a wide variety of temperature ranges, including in the intermediate temperature range of about 100°C to 700°C, and new and improved methods of making these compounds. The present invention also provides new and improved methods for making chalcogenide compounds, including, but not limited to, non-protonated sulfide, selenide and telluride compounds. In one embodiment, the proton conductivity of the compounds is between about 10⁻⁸ S/cm and 10⁻¹ S/cm within a temperature range of between about 50 and 500°C.

13 Claims, 10 Drawing Sheets
Other Publications

* cited by examiner
FIG. 2

Absorbance (A.U.)

Wavenumber (cm⁻¹)

FIG. 2
FIG. 3

Raman shift (cm$^{-1}$)

Arbitrary intensity

- $H_4$
- $H_2.7\text{Cs}_{1.3}$
- $H_2\text{Cs}_2$
- $H_1\text{Cs}_3$
- Cs$_4$
- $H_2.7\text{Rb}_{1.3}$
- $H_2\text{Rb}_2$
- Rb$_4$
- $H_2.7\text{K}_{1.3}$
- $H_2\text{K}_2$
- K$_4$
FIG. 4

Temperature (°C)

\[ \sigma_{\text{d.c.}} (\Omega \cdot \text{cm})^{-1} \]

\[ \frac{1000}{T} (K^{-1}) \]

Hydrous Phases

- \( H_x K_y Ge_z S_{10} \cdot xH_2O \)
- \( H_4 Ge_4 S_{10} \cdot xH_2O \)
- \( H_4 Ge_4 S_{10} \cdot xH_2O \)
- \( Ba(SH)_2 \cdot xH_2O \)
FIG. 5
FIG. 6
FIG. 7
Temperature (°C)

$\sigma_{d.c.} (\Omega \text{cm})^{-1}$

$1000/T (K^{-1})$

**FIG. 10**

- $0.05\text{MoS}_2 + 0.95\text{GeS}_2$
  - $\square$ 12wk liq. $\text{H}_2\text{S}$
  - $\blacksquare$ 6wk liq. $\text{H}_2\text{S}$
  - $\bigcirc$ Batch
COMPOUNDS FOR NOVEL PROTON CONDUCTING MEMBRANES AND METHODS OF MAKING SAME

This application claims the benefit under 35 U.S.C. 119(e) of U.S. Provisional Application No. 60/398,768 filed on Jul. 26, 2002, which is hereby incorporated by reference in its entirety.

STATEMENT OF GOVERNMENT RIGHTS

This invention was made with support of the United States Government under Department of Energy’s Hydrogen Program under Cooperative Agreement No. DE-FC3606GO10531. The Government has certain rights in this invention.

FIELD OF THE INVENTION

The present invention relates to compounds useful for membranes, and, in particular to compounds for novel proton conducting membranes and methods of making same.

BACKGROUND

Hydrogen-based fuel cells are becoming increasingly popular as an alternative to crude oil-based internal combustion engines. Specifically, hydrogen can be converted to electricity through the use of a H₂−O₂ fuel cell. The by-product of this type of fuel cell is water, making this a “green” or environmentally friendly technology. At the heart of the fuel cell is the proton exchange membrane (PEM), which transports protons from the anode to the cathode while providing electronic insulation between them. There are many types of electrolyte materials, each with specific limitations. Generally, such materials either have too low a proton mobility or don’t operate at a high enough temperature to be useful in fuel cells.

Some of the most popular electrolyte materials are polymer exchange membranes, phosphoric acid membranes, and solid oxide membranes. Polymer exchange membranes, or more specifically solid organic polymer poly-perfluorosulfonic acids such as Nafion™, require hydration. However, this limits their operation to temperatures below 100°C, thus requiring the use of expensive noble metal catalysts such as platinum. These electrolytes also suffer from fuel cross-over due to their porous hydrated nature. Phosphoric acid membranes are typically operated from 150°C to 200°C. Being a liquid electrolyte, these membranes suffer from membrane leakage and fuel cross-over problems. They also require the use of expensive platinum catalysts. Solid oxide membranes are typically operated between 700°C to 1000°C, where the use of platinum as an electrode material can be reduced. This temperature range is used to achieve the desired oxide anion conductivity. These membranes being solid in nature do not suffer from fuel cross-over problems. With these current fuel cell membrane materials, however, there remains a temperature region between about 100°C and 700°C that currently no one membrane can provide for optimum performance. In this temperature range, anhydrous proton conductors are desirable.

Thus, what is needed are new compounds for use in proton exchange membranes which are able to operate in a wide variety of temperature ranges, including in the intermediate temperature range of about 100°C to 700°C, and new and improved methods for making these compounds.

SUMMARY

The present invention provides new compounds for use in proton exchange membranes which are able to operate in a wide variety of temperature ranges, including in the intermediate temperature range of about 100°C to 700°C, and new and improved methods for making chalcogenide compounds, including, but not limited to, non-protonated sulfide, selenide and telluride compounds. In one embodiment, the proton conductivity of the compounds is between about 10⁻⁹ S/cm and 10⁻¹ S/cm within a temperature range of between about 50 and 500°C.

In one embodiment, the compound is any cation-modified hydrogen thiogermanate having the Ge₈S₁₀⁺⁺⁺ complex ion. In one embodiment, new protonated compounds made according to the present invention include, but are not limited to hydrogen-modified thiogermanate compounds with the Ge₈S₁₀⁺⁺⁺ complex ion having the formula: H₂Csₓ₋₄Ge₈S₁₀yH₂S·zxH₂O, H₂Rbₓ₋₄Ge₈S₁₀yH₂S·zxH₂O, and H₂Kₓ₋₄Ge₈S₁₀yH₂S·zxH₂O, wherein 0≤x≤4, 0≤y≤1 and z≥0. Such compounds can therefore have either an adamantine-like or double-decker Ge₈S₁₀⁻⁻⁻ structural unit. In one embodiment the compounds are hydrated such that z≥0. In a particular embodiment, x=4 and z=0 and the compound is a hydrated thiogermanic acid, H₂Ge₈S₁₀H₂O. Such a compound can have either a double-decker or adamantine-like structural unit. In one embodiment z=0, x=4 and the compound is the anhydrous thiogermanic acid, H₂Ge₈S₁₀, having an adamantine-like structural unit. In one embodiment the H₂Ge₈S₁₀ has a conductivity value of about 10⁻¹⁰ S/cm (Ωcm⁻¹) at 250°C.

In one embodiment, z=0 and x=4 and the compound is the anhydrous thiogermanic acid, H₂Ge₈S₁₀, having a double-decker structural unit. In one embodiment, the H₂Ge₈S₁₀ has a conductivity value of about 10⁻⁹ S/cm at 360°C.

In one embodiment, the compound is H₂Mo₅S₁₀₋₄₊2x, wherein 1≤x≤2 and 0.5≤z≤1. In a particular embodiment, the compound is a thiomolybic acid, including either anhydrous or hydrated forms. In one embodiment, the thiomolybic acid has a conductivity value of about 0.45 S/cm at 100°C, although the conductivity of this compound is thought to be largely electronic in nature.

Thiogermanic acid can also serve as a proton source material to synthesize other proton conductors. The net result is to create glass/ceramic or ceramic structures with stable S−H groups. IR and Raman spectroscopy have been used to determine the structure of these materials. Structural modifications can also be carried out to maximize the proton concentration and decrease proton-hopping energy.

In one embodiment, various protonated chalcogenide materials are obtained from liquid H₂S, H₂Se and/or H₂Te reactions with a variety of precursor materials. In another embodiment, various crystalline sulfides, selenides and tellurides are also obtained from liquid H₂S, H₂Se and H₂Te reactions, respectively, with a variety of precursor materials. In one embodiment, the precursor compounds are used individually as commercially supplied. In another embodiment, the precursor has a purity in excess of 99 mole %. This includes precursors selected from the group consisting of chalcogenides, halides, and any combination thereof, to produce a protonated chalcogenide or unprotonated crystalline sulfide, selenide and/or telluride. In one embodiment, precursors are selected from the group consisting of an oxide, sulfide, hydroxide, fluoride, chloride, iodide, bromide, and any combination thereof, to produce a thio-acid, a hydrosulfide or a sulfide.
Structural modifications to the precursor can also be carried out to maximize the proton concentration and decrease proton-bonding energy in the membrane material. In one embodiment, the invention provides a method comprising providing a glass phase, ceramic phase or glass/ceramic phase and allowing this precursor phase to protonate in liquid H₂S, H₂Se or H₂Te to produce a protonated membrane material which is chemically and thermally stable. In one particular embodiment, various chalcogenide compounds are solid-state reacted to form a precursor material. This only works if one or more of the precursors produce a protonated chalcogenide upon reacting with liquid H₂S, H₂Se or H₂Te, for example, GeS₂→H₄GeS₄₁₀⁻. Examples of such compounds that can be solid-state reacted include, but are not limited to, various sulfide, oxysulfide, and/or oxide compounds.

In another embodiment, the glassy, glass-ceramic, and/or crystalline precursor materials are tailored to obtain specific crystalline and/or glass-ceramic reaction products. In one embodiment, the resulting glassy, glass-ceramic, or crystalline precursor materials are reacted with liquid H₂S, H₂Se or H₂Te to incorporate protons into the structure. As an example, glasses can be made of Cs₂Ge₅S₈, Rb₂Ge₅S₈, K₂Ge₅S₈ to serve as precursor materials for H₂Cs₂Ge₅S₈ → H₄Rb₂Ge₅S₈₁₀⁻, and H₂K₂Ge₅S₈₁₀⁻, respectively, through reactions with liquid H₂S. In another embodiment, the resulting glassy, glass-ceramic, or crystalline precursor materials can be reacted with liquid H₂S, H₂Se or H₂Te to produce crystalline sulfide, selenide or telluride materials, respectively.

In one embodiment, the reacting step occurs in a closed one-end tube located inside a reaction vessel. In yet another embodiment, the reaction vessel has a reusable sealing mechanism. The method can further comprise placing the precursor in the reaction vessel; drawing a vacuum inside the reaction vessel; cooling the reaction vessel; filling the reactor with the hydrogen sulfide, hydrogen selenide or hydrogen telluride gas; allowing the gas to liquefy and/or solidify; and allowing the reactor to warm to any suitable reaction temperature; and allowing the reaction to proceed wherein a protonated chalcogenide or crystalline sulfide, selenide or telluride is produced. Examples include, but are not limited to, a thio-acid, hydrosulfide or sulfide. In one embodiment, the reaction vessel is cooled. In a particular embodiment, the reaction vessel is cooled to less than about 60°C. In one embodiment, the method further comprises opening the reactor inside an oxygen- and water-free glove box after the reaction is complete. The products produced according to the novel method of the present invention typically have a purity in excess of 92%. Purity can be increased even further by methods described herein.

The net result is to create ceramic or glass/ceramic structures with structural incorporated protons (protonated) or without protons (unprotonated) crystalline sulfides, selenides or tellurides. Some of these protonated materials, such as various thio-acids or sulfide-based materials doped with hydrogen sulfide (H₂S), have been found to be relatively stable in air and water, which is a requirement for H₂—O₂ fuel cell use. (Structural characterization of the obtained protonated materials was carried out using IR and Raman spectroscopies, DSC, TGA, and X-ray diffraction).

The protonated compounds or membrane materials produced according to one embodiment of the novel method of the present invention can easily be converted to membranes, to provide electrochemical characterizations. One method involves pressing fine powders into a pellet. Other methods which are variations of this technique known in the art can also be used. In one embodiment, the well-known method of thin film processing is used to process thin films of the membrane materials. By using carefully controlled glass-ceramic and/or ceramic processing, the anisotropy and texture of the nanostructures of the membrane materials can be tailored to the perpendicular direction of the thin membrane film, thereby optimizing the conductivity. The mechanical properties may also be optimized through the generation of a two-phase glass-ceramic and/or ceramic membrane with a carefully controlled and fine-grained nanostructure.

Ideally, these membranes will be useful in fuel cells at temperatures between about 100°C and 700°C. In other embodiments, the membranes may be useful at temperatures less than 100°C, such as approximately 0°C, particularly in applications such as purifiers. In one embodiment, the invention provides a chemically and thermally stable membrane comprising a glass ceramic, ceramic material or glass/ceramic material adaptable for use in a fuel cell at a temperature of between about -60°C and 700°C, the material having a proton conductivity of between about 10⁻⁶ to 10⁻¹ S/cm. In other embodiments, the proton conductivity may be greater than 10⁻⁵ S/cm, such as about 10⁻⁴ S/cm. In yet other embodiments, depending on the particular application, proton conductivities as low as about 10⁻⁷ S/cm are used, although such conductivities are likely too low for fuel cell applications, but perhaps useful for hydrogen sensors.

Being solid in nature, these membranes are not expected to exhibit fuel cross-over problems. Because of their inherent increased thermal-mechanical stability, the thermal and electrochemical stability of these membranes may be superior to that of Nafion™ and Nafion™-like polymer membranes above 100°C. The compounds and protonated membranes described herein are useful in a variety of applications, as is known in the art, including fuel cell applications, reformers, purifiers, sensors, and the like.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of a square collar reactor connected to external equipment and used for liquid H₂S reactions in an embodiment of the present invention.

FIG. 2 shows far-IR and mid-IR spectra of hydrogen alkali thiogermanates in embodiments of the present invention.

FIG. 3 shows Raman spectra of hydrogen alkali thiogermanates in embodiments of the present invention.

FIG. 4 is an Arrhenius temperature dependent plot of d.c. conductivity values for hydrated forms of specific hydrogen alkali thiogermanates, thigermanic acids, and barium hydrosulfide in embodiments of the present invention.

FIG. 5 is an Arrhenius temperature dependent plot of d.c. conductivity values for the anhydrous heavy alkali hydrosulfides in embodiments of the present invention.

FIG. 6 is an Oak Ridge (Molecular Lab) Thermal Ellipsoid Program (Molecular Modeling) (ORTEP) drawing of the Ge₂S₄₆⁻ anion for the thigermanic acid H₄Ge₂S₄₁₀ showing 30% probability thermal ellipsoids, with H atoms omitted for clarity in an embodiment of the present invention.

FIG. 7 is an Arrhenius temperature dependent plot of d.c. conductivity values for specific anhydrous hydrogen alkali thiogermanates in embodiments of the present invention.

FIG. 8 is an Arrhenius temperature dependent plot of d.c. conductivity values for the thiomolybdic acid in an embodiment of the present invention.
FIG. 9 is an Arrhenius temperature dependent plot of d.c. conductivity values for the 0.14Ga$_2$S$_3$+0.86GeS$_2$+xH$_2$S system in an embodiment of the present invention.

FIG. 10 is an Arrhenius temperature dependent plot of d.c. conductivity values for the 0.05MoS$_2$+0.95GeS$_2$+xH$_2$S system in an embodiment of the present invention.

DETAILED DESCRIPTION

The present invention provides novel compounds for proton conducting membranes and new synthesis methods for producing these and known chalcogenide compounds. The membranes, in turn, are useful as fuel cell electrolyte membranes and other applications. The present invention also provides a new method of making existing compounds, such as thio-acids, sulfides and hydroxysulfides using liquid H$_2$S, and provides for their use in proton conducting membranes. These methods of making include the use of precursors, such as oxide and sulfide precursors, among others. For example, oxide precursors identified as having a thio-acid analog (as defined below) have been tested for conductivity as well as thermal and chemical stability. For example, the reaction of GeO$_2$, with liquid H$_2$S at room temperature produces H$_2$GeS$_2$$_{10}$ at a conductivity of about 10$^{-3}$ S/cm at room temperature, wherein 0<x<9. This compound appears to lose the intercalated H$_2$O at temperatures near 500°C, to yield the thio-germanic acid H$_2$GeS$_2$$_{10}$ or H$_2$GeS$_2$ which have conductivities of about 10$^{-10}$ S/cm at 250°C and 10$^{-8}$ S/cm at 360°C, respectively. Definitions

The term “thio-acid” as used herein, refers to inorganic M$_2$S$_2$H, or H$_2$A-M$_x$S compounds wherein M is a metal or metalloid and A is any metal cation, including, but not limited to, H$_2$GeS$_2$$_{10}$, H$_2$GeS$_2$$_{9}$, H$_2$GeS$_2$$_{8}$, H$_2$GeS$_2$$_{7}$, H$_2$GeS$_2$$_{6}$, H$_2$GeS$_2$$_{5}$, H$_2$GeS$_2$$_{4}$, H$_2$GeS$_2$$_{3}$, H$_2$GeS$_2$$_{2}$, H$_2$GeS$_2$$_{1}$, H$_2$GeS$_2$$_{0}$, Na$_2$SH, K$_2$SH, Rb$_2$SH, Cs$_2$SH, Ba$_2$(SH)$_2$. These compounds can be assigned specific thio-acid names, such as thio-germanic acid, thiomolybdic acid, thioboric (or metathioboric) acid, and so forth. The specific naming for the alkali and alkaline earth metals is slightly different, i.e., potassium hydrosulphide, cesium hydrosulphide, barium hydrosulphide, etc.

The term “sulfur analog” as used herein, refers to oxide compounds in which the oxygen is replaced by sulfur to become a sulfide compound. For example, the sulfur analog of In$_2$O$_3$ is In$_2$S$_3$.

The “thio-acid analog” as used herein, refers to sulfide, oxide, or hydroxide compounds that produce thio-acids as defined above when reacted in solution with liquid H$_2$S.

The term “adamantane-like” as used herein, refers to inorganic materials with a structure unit resembling that of adamantane, which is the organic compound C$_{10}$H$_{16}$. The term “membrane material” as used herein, refers to a “protonated” material or compound, i.e., a material or compound having mobile proton species. Examples include thio-acids and hydroxysulfides. A membrane material is produced when protons are added in a protonation step to the chemical structure of the material. For example, in one embodiment of the present invention a glass, ceramic or glass/ceramic material is reacted with liquid hydrogen sulfide to produce a membrane material.

The term “membrane” as used herein refers to proton-conducting solid electrolytes, which can otherwise be described as a densified or solid thin film of membrane material, typically less than one (1) mm in thickness, used for electrochemical characterization of membrane electrode assemblies (MEA).

The term “material” as used herein refers to a glass, glass/ceramic, or ceramic phase or compound without structurally incorporated protons.

The term “sulfide” as used herein refers to compounds consisting of the element sulfur, and no other chalcogen.

The term “selenide” as used herein refers to compounds consisting of the element selenium, and no other chalcogen.

The term “telluride” as used herein refers to compounds consisting of the element tellurium, and no other chalcogen.

The term “chalcogenide” as used herein refers to compounds consisting of elements from group VIA (Chemical Abstract Service version) of the periodic table including oxygen, sulfur, selenium, tellurium and any combination thereof.

The term “halide” as used herein refers to compounds consisting of the elements from group VIIA (Chemical Abstract Service version) of the periodic table including fluorine, chlorine, bromine, iodine and any combination thereof.

Methods of Preparation

In one embodiment, the method for preparation of protonated chalcogenides, sulfides, selenides and tellurides, according to the present invention includes placing commercial chalcogenide powders of high purity, i.e., typically in excess of 99 mole %, in a closed one-end tube, such as an aluminina tube which, in turn, is placed inside a reaction vessel, i.e., reactor. FIG. 1 provides a simplified cross-sectional view of a typical reactor 100 connected to control equipment, although the invention is not so limited. This reactor design, however, incorporates certain features, such as high temperature re-usable, sealing capability and various other features important for safe operation, particularly when operating at high temperatures.

In the embodiment shown in FIG. 1, the reactor 100 is comprised of an outer metal tube (reactor tube) 102 and a removable inner tube 104 with a sealing unit 105 surrounding the outer circumference of the upper portion of the outer tube 102. In this embodiment, the sealing unit 105 is comprised of a reactor top 106, a shear collar 108 integral with the outer tube 102, a square collar 109 secured by four pairs of bolts 116 and nuts 118 located at each corner of the reactor top 106 and one or more seals 110 located between the top of the outer tube 102 and the reactor top 106, as shown, although the invention is not so limited. Any suitable combination of components in any suitable configuration can be used as the sealing unit 105 as long as the reactor 100 can perform its intended function.

In this embodiment, a vacuum is drawn on the reactor contents through an inlet and outlet line 111 by vacuum means known in the art, although the invention is not so limited. Reactions can also take place under any suitable pressure, including under ambient conditions. In an alternative embodiment, a filler gas, such as helium or nitrogen, is used to produce a higher pressure phase in the reaction product or to increase the reaction rate, depending on the kinetics.

The removal of air to create the vacuum (and the flow of components into the reactor 100) is controlled by a needle valve 112, such as the valves made by Swagelock Co. having offices in Solon, Ohio. Pressure within the reactor 100 is monitored by a pressure gauge 114. After evacuating the contents of the reactor 100, the outer tube 102 is placed inside a liquid nitrogen dewer and cooled to liquid nitrogen temperatures. At this point, H$_2$S, H$_2$Se or H$_2$Te gas (and/or other reactant gases such as boron chloride) may be back-filled into the reactor 100 via the inlet and outlet line 111, again with the pressure monitored by the pressure gauge.
The low liquid nitrogen temperatures allow the gas inside the reactor to obtain a liquid and/or solid phase. The reactor 100 may then be warmed by any suitable means such as under ambient conditions or in a furnace, to a suitable temperature for the reaction to proceed. Reactions can take place under any suitable pressure and temperature, including under ambient conditions.

Preferably, the reactor 100 has a re-usable sealing mechanism. In the embodiment shown in FIG. 1, bolts 116 having nuts 118 are provided at each corner of the square collar 109 to provide the re-usable sealing mechanism. The bolts 116 function to hold the reactor top 106 onto the outer tube 104 via the shear collar 106. Thus, the square collar 109 supplies the load from the bolts 116 to the outer tube 102 via the shear collar 106. In this embodiment, four bolts 116 are used (two shown in FIG. 1), although additional or even fewer bolts can be used, as desired, for different reactor designs. Proper selection of bolt size and number is important, however, to ensure adequate strength for the applied load from the square collar 109. In other words, the yield strength of the bolts 116 must be greater than the applied load exerted by the gaseous phase on the square collar 109. In most embodiments utilizing this type of re-usable sealing mechanism, the bolts 116 will have a diameter of at least about 0.25 in and a length of about 0.75 to six (6) in, although the invention is not so limited. In one embodiment, 0.375-in-diameter bolts, having a length of about 3.5 in are used when the outer tube 102 has an inside diameter of about one (1) in.

Any suitable material that can withstand high temperatures and is corrosion resistant to H₃S, H₂Se and H₂Te and sulfide, selenide and/or telluride vapors can be used for the outer tube 102. Preferably the material used is economical and easily machineable. In one embodiment, stainless steel 316 is used. This material provides adequate corrosion resistance up to approximately 400° C. and is easily machined. At higher temperatures the reaction with the iron becomes significant and so materials must be even more carefully selected. In such embodiments, a liner or coating made from a metal, (e.g., tantalum), ceramic (e.g., aluminum oxide, Al₂O₃), or amorphous material (e.g., vitreous carbon or silica) is used to line the outer tube 102.

The outer tube 102 can have any suitable thickness. In a particular embodiment, the outer tube 102 has a wall thickness of approximately 0.2 in. Reactor hoop stress (i.e., the stress in the reactor tube wall acting circumferentially in a plane perpendicular to the longitudinal axis of the reactor tube) is produced by the pressure of the gaseous reactants and is normally used as the limiting stress for safety calculations, as is known in the art.

The size of the outer tube 102 can also vary according to the reactor design. For most experimental operations, the outer tube 102 has an inside volume of between about 50 and 100 mL. In one embodiment, the outer tube 102 has a volume of about 78 mL.

The inner tube 104 which holds the sample can be made from any suitable material able to withstand reaction conditions. In one embodiment the inner tube 104 is made from alumina, silica, polytetrafluoroethylene (i.e., Teflon®). In one embodiment, the tube is an alumina tube designed to be more securely secured inside the inner volume of the outer tube 104 as shown in FIG. 1.

The shear collar 108 of FIG. 1 is round in geometry, although the invention is not so limited. The shear collar 108 can have any suitable thickness as long as it can resist the shear forces to which it is exposed during operation. In embodiments that operate at the vapor pressure of H₂S at room temperature, the shear collar 108 is at least about 0.25 in thickness. In a particular embodiment, the shear collar 108 has a thickness of about 0.625 in. In other embodiments, a shear collar 108 is not required, and the reactor top 106 can be attached to the outer tube 102 directly through the bolts 116 or other mechanical sealing mechanisms known in the art.

Any suitable type of seal 110 can be used to seal the reactor 100. In one embodiment, the seal 110 is an o-ring designed for temperatures below about 230° C. In a particular embodiment the seal is a Teflon® brand fluorinated ethylene propylene (FEP) o-ring. In another embodiment, the seal 110 is a copper washer-carbon disk composite gasket for higher temperature operation. In yet another embodiment, the seal is a Viton® brand o-ring which are known to be useful for room temperature reactions which can last up to four weeks.

In operation, a vacuum is first drawn inside the reactor 100, which is then cooled by any suitable means, such as with liquid nitrogen as described above. The reactor is then typically filled with H₂S, H₂Se or H₂Te gas, such as 99.5% pure gas manufactured by Matheson Tri-Gas Co., having offices in Montgomeryville, Pa. The reactions can take place at room temperature where liquid H₂S, H₂Se or H₂Te is present in the reactor under its own vapor pressure. In other embodiments, the temperatures can be about 78 to 230° C. The reactants and/or products may be in solution/suspension with the liquid H₂S, H₂Se or H₂Te. After the designated reaction time, resulting H₂S—H₂O solutions may be evaporated through an aqueous solution of NH₄OH to obtain NH₄SH. The NH₄SH solution may then be reacted with H₂O₂ to obtain NH₄OH and S₈ according to the reactions:

\[ \text{H}_2\text{S}+\text{NH}_4\text{OH}→\text{H}_2\text{O}+\text{NH}_4\text{SH} \]

In another embodiment H₂S, H₂Se or H₂Te from the resulting reaction solution is recycled by implementing drying materials such as silica gel, anhydrous calcium chloride, such as calcium chloride made by DampRid, Inc., having offices in Orlando, Fla. In another embodiment anhydrous calcium sulfate made by W.A. Hammond Drierite Co. LTD. having offices in Xenia, Ohio, is used. In yet other embodiments, selective pressure swing absorption (PSA) materials or molecular sieves including 3 Å potassium zeolite, or appropriate cold traps (−60° C.<T<0° C.) for H₂O are used to recycle the H₂S, H₂Se or H₂Te.

In one embodiment, after removal of the H₂S, H₂Se or H₂Te solution, the reactor 100 is removed from the control equipment and opened inside an oxygen and water free glove box (<5 ppm) where mass measurements of the resulting product can be recorded as a function of time. Interrelated H₂O may take up to five (5) days to dissipate at room temperature. However, vacuum drying or heating the samples to about 100° C. with about 100 mTorr vacuum may be used to speed this process down to about one (1) day in duration. Water in the resulting product may be identified by infrared spectroscopy, with an O—H stretching mode between about 3300 and 3600 cm⁻¹ and a H—O—H bending mode around 1620 cm⁻¹. Thio-acids and hydrosulfides may be identified from the presence of the S—H stretching mode around 2500 cm⁻¹ (assuming an electronic insulator material). Further characterization including Raman spectroscopy, thermogravimetric analysis, differential scanning calorimetry and X-ray diffraction may be performed to identify the product.

Methods of increasing the solubility and/or reaction rate include: increasing the reaction temperature or adding small...
Methods of purifying the products may include recycling and reusing the H₂S, H₂Se or H₂Te liquid with longer rection times. Examples of specific syntheses are found in the Examples.

The novel methods of the present invention comprise reacting liquid H₂S, H₂Se or H₂Te with chalcogenide or halide precursor materials to create protonated chalcogenides, sulfides, selenisides and tellurides. The protonated chalcogenides may then be mixed thermally with other chalcogenide materials in a suitable mixing container to produce a glass material (e.g., if cooled rapidly) or ceramic material (e.g., if cooled slowly). In one embodiment, the suitable reacting container is an evacuated silica tube. In other embodiments, the mixing container is a carbon crucible in a water and oxygen-free glove box or any other means known to those skilled in the art. It is also possible to react various chalcogenide compounds in a silica tube to produce a glass, glass-ceramic or ceramic material, and then react that product with liquid H₂S, H₂Se or H₂Te. This is possible, for example, when one or more of the chalcogenides produces a chalcogenide-acid or hydrochalcogenide, e.g., GeS₂ → H₂Ge₂S₄. For example, the ceramic material BaGe₃ may protonate in liquid H₂S to produce a chemically and thermally stable membrane material or material useful in membrane applications.

Various chalcogenide precursors, as well as halide precursors, and any combination thereof, can be reacted with liquid H₂S, H₂Se or H₂Te at room temperature for various lengths of time. As described in the examples below, 25 oxide and hydroxide precursors were tested, although it is likely many other types of precursors can be used to produce useful thio-acids other than the thio-acids produced herein. Referring to the examples, however, of the 25 tested, 14 formed sulfide products in solution with liquid H₂S, while the remaining 11 appeared to be relatively inert. Of these 14, seven (7) formed thio-acids or hydroxysulfides, namely:

<table>
<thead>
<tr>
<th>Oxide/Hydroxide Precursors</th>
<th>Sulfide Precursors</th>
<th>Bromide/Chloride/Iodide</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeO₂ → H₂Ge₂S₄</td>
<td>GeS₂ → H₂Ge₂S₄</td>
<td>BaBr₂ → HBS₂</td>
</tr>
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<td>H₂Ge₂S₄ → H₂Ge₄S₁₀</td>
<td>K₂₄Ge₂S₁₀ → K₂₄Ge₂S₁₀</td>
<td>BC₃ → HBS₂</td>
</tr>
<tr>
<td>MoO₃ → 2MoS₂ or 3H₂S</td>
<td>H₂X₄ → H₂Mo₂S₅</td>
<td>Sn₂ → no reaction</td>
</tr>
<tr>
<td>H₂MoS₄ → NaSH</td>
<td>Rb₂₄Ge₂S₁₀ → Rb₂₄Ge₂S₁₀</td>
<td></td>
</tr>
<tr>
<td>KO₂ → K₂S</td>
<td>Rb₂₄Ge₂S₁₀ → Rb₂₄Ge₂S₁₀</td>
<td></td>
</tr>
<tr>
<td>Rb₂₄Ge₂S₁₀ → Rb₂₄Ge₂S₁₀</td>
<td>Na₂₄Ge₂S₁₀ → Na₂₄Ge₂S₁₀</td>
<td></td>
</tr>
<tr>
<td>Cs₂₄Ge₂S₁₀ → Cs₂₄Ge₂S₁₀</td>
<td>Ba₂₄Ge₂S₁₀ → Ba₂₄Ge₂S₁₀</td>
<td></td>
</tr>
<tr>
<td>Ba(OH)₂ → Ba(SH)₂ or H₂O</td>
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<td></td>
</tr>
<tr>
<td>Sn₂O₅ → Sn₂S₃</td>
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</tr>
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<td></td>
</tr>
<tr>
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<td>In₂O₃ → In₂S₃</td>
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</tr>
<tr>
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<td>W₂O₅ or WS₂</td>
<td></td>
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<tr>
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<td></td>
</tr>
<tr>
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</tr>
<tr>
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<td></td>
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</tr>
<tr>
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<td></td>
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<tr>
<td>H₂BO₃ → no reaction</td>
<td>Ce₂O₅ → no reaction</td>
<td></td>
</tr>
<tr>
<td>H₂BO₃ → no reaction</td>
<td>B₂O₃ → no reaction</td>
<td></td>
</tr>
</tbody>
</table>

Table 1 summarizes the various precursor reactions with liquid H₂S that were tested herein, although the invention is not so limited. Various characterizations were done on each, which included total mass increase, Raman, IR, TGA, DSC, and XRD. As is discussed herein, the present invention further provides at least two new thio-acids, namely, thio-germanic acid and thionomolyblic acid, formed via the methods described herein. It is expected that other novel thio-acids may also be formed according to the methods of the present invention. Detailed data from these experiments can be found in the Examples below.

---

**Table 1**

<table>
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</table>
As noted above, the present invention provides, in one embodiment, measurable proton conductivity in hydrous and anhydrous chalcogenide samples and further demonstrates thermal and chemical stability. In developing new proton conducting membrane materials, it is important to test the diffusion behavior of protons in the respective materials. Proton conducting samples can be tested using a.c. impedance measurements. Proton self-diffusion coefficients of these proton conducting samples can be determined from H\textsuperscript{+}-NMR spin-echo pulse sequences with magnetic field gradient pulses. Thermal and chemical stability of these proton conducting samples can be measured using thermogravimetric analysis where non-reactive atmospheres, such as nitrogen or argon, can be used to determine the thermal stability of the sample, and reactive atmospheres of oxygen and water vapor can be used to determine the chemical stability of the sample. Thereafter, for samples possessing both good proton conductivity and thermal and chemical stabilities, a working membrane can be fabricated to which a pressure differential of hydrogen can be applied.

In all the Examples described herein, various protonated sulfide materials were obtained from liquid H\textsubscript{2}S reactions with a variety of precursor materials. Various crystalline sulfide materials were also obtained from liquid H\textsubscript{2}S reactions with a variety of precursor materials. Precursor materials tested herein include sulfides (Examples 2-5), oxides (Examples 2, 3, 5 and 6) and hydroxides (Example 1). Additionally, the glassy and/or crystalline precursor materials were tailored to obtain specific crystalline and/or glass-ceramic reaction products, as described in Examples 4 and 5. Specifically, various sulfide and/or oxide compounds were solid state reacted, e.g. inside evacuated silica tubes. (Examples 2, 4 and 5). In other tests, the compounds were used individually as commercially supplied. (Examples 1-3 and 6). The resulting glassy, glass-ceramic, or crystalline precursor materials were then reacted with H\textsubscript{2}S to incorporate S—H bonds into the structure and produce membrane materials.

Generally, the reaction time was found to be very dependent on the water content, both impurity or added, in the H\textsubscript{2}S. Additionally, the reaction temperature can be increased, such as was done in Example 2, to increase the reaction rate. After the designated reaction time, the resulting H\textsubscript{2}S—H\textsubscript{2}O solution was evaporated through an aqueous solution of NH\textsubscript{4}OH. In many cases, such as in Examples 2, 4 and 6), the initial reaction product was a protonated sulfide material, an unprotonated reaction product obtained from longer reaction times. The resulting reaction products had various impurity and/or intercalated materials, depending on the starting precursor materials, e.g., H\textsubscript{2}S and H\textsubscript{2}O. Vacuum drying or other suitable distillation and/or precipitation reactions were used to purify the reaction products.

FIG. 2 shows the far-IR and mid-IR spectra of hydrogen alkali thiogermanates in various embodiments of the present invention. The far-IR presents vibrational bands of the adamantan-like unit cage, whereas the mid-IR presents bands attributed to S—H stretching mode. A broad mode at about 2250 cm\(^{-1}\) is observed for the cesium modified systems suggesting strong hydrogen bonding of intercalated H\textsubscript{2}S. Details of these compounds are discussed below in Examples 2 and 4.

FIG. 3 shows Raman spectra of hydrogen alkali thiogermanates in various embodiments of the present invention. The lower frequency (<500 cm\(^{-1}\)) vibrational bands are consistent with adamantan-like Ge\textsubscript{x}S\textsubscript{y}H\textsubscript{z} anions terminated by a mix of hydrogen and alkali cations. In the higher frequency region, a S—H stretching mode is observed about 2500 cm\(^{-1}\). Details of these compounds are discussed below in Examples 2 and 4.

Uses
As noted above the protonated membranes containing the compounds described herein are useful in cell fuel applications. However, as those skilled in the art understand, the ability of a membrane to transport protons is also useful in hydrogen reformers, purifiers and sensors.

The present invention will be further described in the following non-limiting Examples:

EXAMPLE 1

Reactor
A reactor similar to the reactor shown in FIG. 1 was used for all Examples described herein. This particular reactor was made of stainless steel type 316 material. Bolt sizes of 0.375-in diameter and 3.5 in length were used. The outer tube (102 in FIG. 1) had an inside diameter of approximately 1.05 in and a wall thickness of about 0.23 in. A Teflon® brand FE-P o-ring was also used as the seal (110) between the outer tube and the square top (102 and 106, respectively, in FIG. 1). An alumina tube (104) was used to hold the samples and the total free volume inside the reactor, i.e., free volume of the outer tube 102 with the inner tube 104 inside was approximately 72 ml (i.e., the volume of the outer tube 102 was 78 ml, with the inner alumina tube 104 having a six (6) ml volume.

Structural Characterization
Structural investigations of the reaction products for all Examples were performed using a Bruker IFS 66/S Far-IR and Mid-IR spectrometer and a Bruker RFS 100/S Raman spectrometer. Various vibrational modes may be IR, Raman, or active with both spectroscopy methods. Additionally, XRD was performed on single crystals and/or powders. Structural investigations before and after exposure were used to determine stability with H\textsubscript{2}O and O\textsubscript{2}. Exposure time varied from a few hours to one month depending on reactivity of the select samples.

Conductivity Measurement
a.c. impedance data was collected on the protonated reaction products, i.e., membrane materials, in all Examples in the same manner. Additionally, the conductivity of the precursor materials was measured to determine if the protonation has indeed increased the conductivity. A Gamry PC4/750 potentiostat was used in the frequency range of 0.2 Hz to 100 kHz using 0.5 V amplitude on pressed powder samples. Hardened steel blocking electrodes pressed into a Teflon sleeve sealed the cooled hydrous and anhydrous powder samples for liquid nitrogen temperatures up to 290° C. An alumina tube was used to contain anhydrous powder samples for higher temperature measurements up to 500° C. Sixty (60) mg to 100 mg of each sample was pressed inside the ¼ inch ID Teflon sleeves or alumina tubes using about 82 kp/s of pressure with pellet thickness ranging from 0.6 mm to one (1) mm. Constant contact pressure was maintained on the pellet/electrode assembly during the measurement by a metal frame insulated from the electrodes with Teflon or alumina. During the measurement, the sample was contained in a silica cell that maintained about one atmosphere pressure of helium. Cold measurements were performed by dipping the bottom of the cell in liquid nitrogen and allowing the liquid nitrogen to slowly evaporate over a period of about 12 hours; data was collected every 5° C. while the cell warmed to room temperature. Above room temperature, the bottom of cell was placed in a custom-built crucible furnace. Data was collected after the sample temperature stabilized for half an hour using increments of 10° C. or 15° C.
Thermal Stability

A Perkin Elmer Thermogravimetric Analyzer TGA 7 (TGA) and a Perkin Elmer Differential Scanning Calorimeter Pyris 1 (DSC) were used to determine the thermal stability of the protonated reaction products in all Examples, including decomposition, sublimation, crystallization, and glass transition temperatures. For purposes of these experiments, the thermal stability limit is defined as the maximum temperature in an inert atmosphere with no decomposition or sublimation. Nitrogen was used as the sample purge gas to prevent any oxidation reactions for all experiments. For DSC experiments 5 mg to 15 mg of fine powder was sealed inside crimped aluminum sample pans. For TGA experiments about 25 mg of each sample was placed inside an aluminum sample pan. A heating rate of 10° C per minute was used for all thermal stability experiments.

Alkaline and Alkaline Earth Hydrosulfides from Hydride Precursors

In this test, the anhydrous alkali hydrosulfides of NaSH, KSH, RbSH, and CsSH and the hydrated alkaline earth hydrosulfide of Ba(SH)2 were synthesized from liquid H2S reactions with the corresponding hydrides (0.2 to 3 g) of NaOH, KOH, RbOH, CsOH, and Ba(OH)2 respectively. Typically, these reactions were done at room temperature (about 25°C) with liquid H2S (7 to 21 g) at its vapor pressure of about 267 psia for a period of weeks (14 to 21 days).

The reaction routes may be written as follows:

\[ \text{MOH}_{2x} + \text{H}_2\text{S} \rightarrow \text{M} \text{SH} + \text{H}_2\text{O} (\text{M} = \text{Na, K, Rb, Cs}) \]

\[ \text{Ba(OH)}_{2x} + \text{H}_2\text{S} \rightarrow \text{Ba(SH)}_{2x} + \text{H}_2\text{O} (\text{2x} = \text{y}) \]

wherein 0 ≤ x ≤ 8 and 0 ≤ y < 10.

The removal of the intercalated water from the reaction products for the alkali hydrosulfides may be facilitated through vacuum drying, i.e. heating the samples about 100°C with about 100 mTorr vacuum for a day. The products may be further purified (if so desired) by repeating the H2S reaction procedure. In contrast, the intercalated water for barium hydrosulfide proved to be difficult to remove, without decomposing the hydrosulfide product. However, anhydrous Ba(SH)2 may be produced from liquid H2S reactions with BaS. It is worth mentioning that this processing route may have potential application for producing relatively pure hydrosulfide products at room temperature and these products are not readily available commercially.

The d.c. conductivity values as a function of temperature of the hydrated barium hydrosulfide phase, which is closely linked to the presence of the intercalated water for fast proton conductivity, can be observed between 85°C to 120°C. See, for example, FIG. 4, which is an Arrhenius temperature dependent plot of d.c. conductivity values for hydrated forms of specific hydrogen alkali thiogermanates, thiogermanic acids, and barium hydrosulfide in various embodiments of the present invention. Fast proton conductivity is realized below about 100°C, associated with presence of intercalated H2O.

The d.c. conductivity of the anhydrous alkali hydrosulfide phases are believed to be attributed to a free-proton transport mechanism and related to specific polymorphs as a function of temperature. See, for example, FIG. 5 which is an Arrhenius temperature dependent plot of d.c. conductivity values for the heavy alkali hydrosulfides in embodiments of the present invention. The decrease in conductivity for KSH and RbSH between 110°C to 130°C is associated with a first order phase transition. At higher temperatures, decomposition is observed and alkali mobility is suspected (not shown). As FIG. 5 shows, thermal decomposition is observed about 105°C for Ba(SH)2 and about 550°C for the heavy alkali sulfides.

EXAMPLE 2

Thiogermanic Acids from Oxide and Sulfide Precursors

All test conditions were as described above in Example 1. However, in this test, anhydrous thiogermanic acids H3Ge2S10 and H3Ge3S12 were synthesized by reacting glassy Ge2S4 (0.5 g) or quartz-type GeO2 (0.5 to 3 g) with gaseous and liquid H2S. Typically, these reactions were done at room temperature (about 25°C) with liquid H2S (7 to 21 g) at its vapor pressure of about 267 psia. Higher temperature reactions, e.g., ~200°C, were also performed with gaseous H2S. The reactions were performed with and without the addition of water (0 to 57 mg) to the H2S. The reaction products were found to vary as a function of the reaction time (3 to 84 days) and water content. Two reaction routes are noted: anhydrous and hydrous.

The anhydrous reaction route may be written as follows:

\[ \text{4GeS}_2 \text{(glassy)+2H}_2\text{S} \rightarrow \text{H}_3\text{Ge}_2\text{S}_10(\text{adamantane-like})+4\text{GeS}_2(\text{THF})_2 \]

whereas the hydrous reaction route may be written:

\[ \text{4GeO}_2 \text{(quartz-type)+10H}_2\text{S} \rightarrow \text{H}_3\text{Ge}_3\text{S}_12(\text{adamantane-like})\times\text{H}_2\text{O} \]

wherein 0 ≤ x ≤ 8 and 0 ≤ y ≤ 10.

The resulting reaction products were the adamantane-like H3Ge2S10 thiogermanic acid, the double-decker H3Ge3S12 thiogermanic acid, and the high temperature 3-D α-GeS2. See FIG. 6, which is an ORTEP drawing of the GeS102− anion for the thiogermanic acid H3Ge2S10 showing 50% probability thermal ellipsoids, with H atoms omitted for clarity. The hydrous reaction route initially produced hydrous H3Ge2S10 × xH2O phases for both the adamantane-like and double-decker structural units. The d.c. conductivity values as a function of temperature of these hydrous phases were closely linked to the presence of the intercalated water (See FIG. 4). In fact, fast proton conductivity was observed between 0°C to 10°C.

The d.c. conductivity of the anhydrous phases is believed to be attributed to a free-proton transport mechanism. See FIG. 7, which is an Arrhenius temperature dependent plot of d.c. conductivity values for specific hydrogen alkali thiogermanates in various embodiments of the present invention. Lines are drawn as guides for the eyes. As FIG. 7 shows, the adamantane-like H3Ge2S10 thiogermanic acid decomposed at approximately 250°C, whereas the double-decker H3Ge3S12 thiogermanic acid decomposed at approximately 360°C.

EXAMPLE 3

Thiomyloic Acid from Oxide and Sulfide Precursors

All test conditions were as described above in Example 1. However, in this test, a thiomyloic acid, H3MoS6 was synthesized from both hydrous and anhydrous reactions with liquid H2S, wherein 1 ≤ x ≤ 2 and 0.5 ≤ y ≤ 1. The hydrous and anhydrous reactions were performed using MoO3 (0.75 g) and MoS2 (0.75 g), respectively, as precursor materials with the commercially supplied H2S. These reactions were done at room temperature (about 25°C) with liquid H2S (about 17 g) at its vapor pressure of about 267 psia. The resulting reaction product appeared to be independent of reaction time (14 to 84 days).
The anhydrous and hydrous reaction routes may be generally written, respectively, as follows:

\[
\begin{align*}
\text{MoS}_2 + (\text{e} + 2\text{H}_2\text{S} &\rightarrow \text{H}_2\text{MoS}_2 + 2\text{H}_2 \\
\text{MoO}_3 + (\text{e} + 2\text{H}_2\text{S} &\rightarrow \text{H}_2\text{MoS}_2 + 2\text{H}_2\text{O} + (1/2 - 2\text{H}_2\text{S})
\end{align*}
\]

wherein \(1 \leq \delta \leq 2\) and \(0.5 \leq \xi \leq 1\).

The thiomolybdic acid reaction product appears to not only be an excellent proton conductor, but an excellent electron conductor as well (with a Fermi level within the d band gap) up to about 1170°C. See FIG. 8, which is an Arrhenius temperature dependent plot of d.c. conductivity values for the thiomolybdic acid in an embodiment of the present invention. Thermal decomposition was observed above approximately 950°C, a corresponding decrease in conductivity was associated with the loss of the mobile proton species as H_2S. This compound may be dimolybd-

The higher conductivity values associated with longer reaction times are a result of higher proton concentrations and increased bonding energies. See, for example FIGS. 9 and 10. FIG. 9 is an Arrhenius temperature dependent plot of d.c. conductivity values for the 0.14Ga_2S_3 + 0.86GeS_2 + xH_2S system in an embodiment of the present invention. Higher proton conductivity values and more protonation, \(x\), were realized with increased reaction time with liquid H_2S. The glassy precursor became a glass ceramic protonated product or membrane material after the reaction. FIG. 10 is an Arrhenius temperature dependant plot of d.c. conductivity values for the 0.05MoS_2 + 0.95GeS_2 + xH_2S system in an embodiment of the present invention. Higher proton con-

EXAMPLE 4

Hydrogen Alkali Thiogeremanates from Sulfide Precursors

All test conditions were as described above in Example 1. However, hydrogen alkali thiogeremanates were synthesized by reacting the respective alkali thiogermanate glass (0.5 to 0.75 g) or adamantane-like crystalline phase (0.5 to 0.75 g) with liquid H_2S. The resulting reaction product was dependent on reaction time (4 to 28 days). Shorter times produce adamantane-like protonated cage structures, whereas longer times produced unprotonated high temperature 3-D α-GeS_2 crystal structures.

The anhydrous reaction route may be written as follows:

\[
\begin{align*}
\text{M}_2\text{GeS}_{10} &\rightarrow (\text{adamantane-like, glassy}) + \text{H}_2\text{S} \rightarrow \text{M}_2\text{GeS}_4 \\
\text{M}_2\text{GeS}_{8} &\rightarrow (\text{adamantane-like, crystal}) + \text{H}_2\text{S} \rightarrow \text{M}_2\text{GeS}_4
\end{align*}
\]

wherein \(0 \leq \delta \leq 4\), \(0 \leq \gamma \leq 0.5\), \(0 \leq \alpha \leq 1\), and \(0 \leq \zeta \leq 1/2\).

For shorter reaction times, the reaction product was hydrogen alkali thiogermanate. These protonate phases were observed to thermally decompose around about 175°C. Below the decomposition temperature, the ionic conductivity was attributed to a free-proton transport mechanism. (See FIG. 7). Ionic conductivity is shown in regions with distinguishable proton mobility, and higher temperature mobility may be attributed to the alkali. Anomalous behavior is a function of thermal history and the decomposition process.

EXAMPLE 5

Composite Proton Conductors from Oxide and Sulfide Precursors

All test conditions were as described above in Example 1. However, in this test, protonated glass-ceramics and ceramics were produced from liquid H_2S reactions with various glassy and crystalline GeS_2 compositions. Specific examples include 0.14 Ga_2S_3 + 0.86 GeS_2 and 0.05 MoS_2 + 0.95 GeS_2 materials that were synthesized in evacuated silica tubes. These materials (about 0.5 g) were then reacted at room temperature (about 25°C) for extended time periods (14 to 84 days) with H_2S (8 to 17 g) at its vapor pressure of about 267 psi.

The resulting products had S—H groups formed associated with the GeS_10^{2+} and Mo—S non-bridging sites. The
samples; all data reported here is predominately ionic in nature, except the thiomolybdc acid. Physical properties of the membrane materials have been determined, including decomposition, sublimation, crystallization, and glass transition temperatures. Structural comparisons have been used to examine stability with exposure to H₂O and O₂.

Although the present invention has been described in considerable detail with reference to certain preferred versions thereof, other versions are possible. Therefore, the spirit and scope of the appended claims should not be limited to the description of the preferred embodiments contained herein.

What is claimed is:
1. A compound comprising:
   \[ H_{x}O_{y}Ge_{z}S_{10}H_{2}S_{2}H_{2}O, \ H_{x}Rb_{y}Ge_{z}S_{10}H_{2}S_{2}H_{2}O, \ H_{x}K_{y}Ge_{z}S_{10}H_{2}S_{2}H_{2}O, \]
   wherein
   \( 0 < x \leq 4; \)
   \( 0 \leq y \leq 1; \) and
   \( z \geq 0. \)
2. The compound of claim 1 wherein \( x = 4. \)
3. The compound of claim 1 wherein \( z = 0. \)
4. The compound of claim 3 comprising a compound having a double-decker structural unit.
5. The compound of claim 4 wherein the double-decker compound is \( H_{2}Ge_{2}S_{10}. \)
6. The compound of claim 3 comprising a compound having an adamantane-like structural unit.
7. The compound of claim 6 wherein the adamantane-like compound is \( H_{4}Ge_{2}S_{10}. \)
8. The compound of claim 1 wherein \( z > 0. \)
9. The compound of claim 8 comprising a compound having a double-decker structural unit.
10. The compound of claim 9 wherein the double-decker compound is \( H_{4}Ge_{2}S_{10}H_{2}O \) wherein \( 0 < x < 9. \)
11. The compound of claim 8 comprising a compound having an adamantane-like structural unit.
12. The compound of claim 11 wherein the adamantane compound is \( H_{4}Ge_{2}S_{10} \) wherein \( 0 < x < 9. \)
13. The compound of claim 1 wherein the proton conductivity is between about \( 10^{-9} \) S/cm and \( 10^{-1} \) S/cm within a temperature range of between about –50 and 500°C.
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

On the Title page, in item (54), in “Title”, after “MEMBRANES” delete “AND METHODS OF MAKING SAME”.


On page 2, in item (56), References Cited, under “Other Publications”, in column 1, line 24, delete “(HBS2)3” and insert - -(HBS)2. - -, therefor.

On page 2, in item (56), References Cited, under “Other Publications”, in column 2, line 24, delete “Reaction,” and insert - - Reactions, - -, therefor.

On page 2, in item (56), References Cited, under “Other Publications”, in column 2, line 36, delete “poly-perfluorosulfonate” and insert - - poly-perfluorosulfonate - - , therefor.

In column 1, lines 2-3, after “MEMBRANES” delete “AND METHODS OF MAKING SAME”.

In column 5, line 24, delete “10³” and insert - - 10³ - -, therefor.
In column 7, line 24, delete “0.25 in and” and insert - - 0.25 inches and - -, therefor
In column 8, line 1, delete “in in” and insert - - inches in - -, therefor.
In column 10, line 2, delete “CsSH” and insert - - CsSH, - -, therefor.
In column 10, line 2, insert - - or - - before “Ba(SH)xH2O”.
In column 10 (Table 1, Col. 1), line 5, delete “MoO3” and insert - - MoO3 - -, therefor.
In column 12, line 16, delete “3.5 in in” and insert - - 3.5 inches in - -, therefor.
In column 12, line 18, delete “1.05 in and” and insert - - 1.05 inches and - -, therefor.
It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

In column 13, lines 17–18, delete “Alkali and Alkaline Earth Hydrosulfides from Hydroxide Precursors” and insert the same as Sub heading.
In column 16, line 32, delete “respectively.” and insert - - respectively. - - , therefor.

Signed and Sealed this

Twenty-ninth Day of August, 2006

JON W. DUDAS
Director of the United States Patent and Trademark Office