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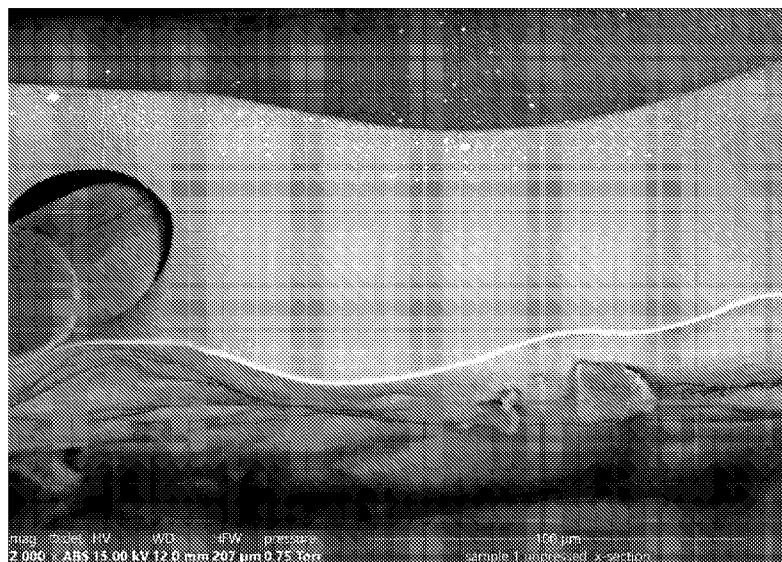
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MADE THEREFROM

FIG. 1



(57) Abstract: The present invention relates to a composition comprising about 90% to about 99.99% by weight of one or more non-crosslinked fluorinated sulfonyl fluoride polymers and about 0.01% to about 10% by weight of one or more precious metal catalyst, based on the total weight of the composition, where the one or more precious metal catalyst is uniformly distributed throughout the one or more non-crosslinked fluorinated sulfonyl fluoride polymer. Such a composition may be formed, for example by extrusion, into a cation exchange precursor and, after treatment, a cation exchange membrane. The resulting films and membranes have precious metal catalyst uniformly distributed throughout the layer of catalyst-containing polymer.



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TITLE

COMPOUNDED FLUORINATED SULFONYL FLUORIDE POLYMERS AND ION
EXCHANGE MEMBRANES MADE THEREFROM

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority of U.S. Provisional Application No. 63/454,927 filed March 27, 2023, and of U.S. Provisional Application No. 63/527,614 filed July 19, 2023, the disclosures of which are incorporated herein by reference in their entirety.

FIELD OF THE INVENTION

[0002] The present invention describes compounded fluorinated sulfonyl fluoride polymers, ion exchange membrane precursors, ion exchange membranes, and the processes of making such materials. The compounded polymers and ion exchange membranes have improved gas recombination catalyst dispersed throughout the resin and can be used to form electrolytic systems, including catalyst coated membranes, fuel cells, and water electrolysis systems.

BACKGROUND

[0003] Precious metal compounds can be added into electrolytic systems as a gas recombination catalyst (GRC) to help reduce hydrogen (H_2) in oxygen that crosses through the cation exchange membrane during operation. Because of the expense and resource limitations of these precious metal compounds, a key goal is to optimize the reduction in hydrogen crossover while minimizing the amount of precious metal compound used.

[0004] The most common technique used in the industry is to cast a dispersion of ionomer (such as NafionTM ion exchange resin dispersion) with precious metal catalyst particles in the dispersion. This dispersion is cast onto a backer or into a reinforcement, and then the solvent is removed to leave an ionomer membrane with GRC behind. However, the downside to this approach is that there is a chance for GRC particles to agglomerate during the casting as well as the final cast membrane having low polymer entanglements and high swelling. Casting processes are described in US2021/0135244 and US2008/0161429, for example.

[0005] Other processes of incorporating a GRC into a membrane include chemically treating the membrane before swelling the membrane and immersing it in a GRC solution, such as that suggested in US2008/0003479. However, this process involves multiple steps and liquid media, which is not ideal for product efficiency. Also, the process does not allow for precise configuration and placement of the GRC material.

SUMMARY

[0006] The present invention provides a novel way to strategically place a GRC in an extruded cation exchange membrane via processing methods. One discovery of the invention is that strategic placement of the GRC provides a performance advantage, product configuration advantage, optimizes polymer entanglement and membrane swelling, limits the amount of raw materials required, and reduces the post-processing steps to incorporate a GRC. The present invention describes compounded fluorinated sulfonyl fluoride polymers, ion exchange membrane precursors, ion exchange membranes, and the processes of making such materials. The compounded polymers and ion exchange membranes have improved dispersion of gas recombination precious metal catalysts throughout the resin and can be used to form electrolytic systems, including catalyst coated membranes, fuel cells, and water electrolysis systems.

[0007] The present invention relates to a composition comprising about 90% to about 99.99% by weight of one or more non-crosslinked fluorinated sulfonyl fluoride polymers and about 0.01% to about 10% by weight of one or more precious metal catalyst, based on the total weight of the composition, where the one or more precious metal catalyst is uniformly distributed throughout the one or more non-crosslinked fluorinated sulfonyl fluoride polymer. The present invention also relates to a cation exchange membrane precursor comprising at least one proton exchange precursor layer, where the at least one proton exchange precursor layer comprises about 90% to about 99.99% by weight of one or more non-crosslinked fluorinated sulfonyl fluoride polymers and about 0.01% to about 10% by weight of one or more precious metal catalysts, based on the total weight of the composition, where the one or more precious metal catalyst is uniformly distributed throughout the at least one proton exchange precursor layer. The present invention further relates to A cation exchange membrane comprising at least one cation exchange layer, where

the at least one proton exchange layer comprises about 90% to about 99.99% by weight of one or more non-crosslinked fluorinated sulfonic acid polymers and about 0.01% to about 10% by weight of one or more precious metal catalysts, based on the total weight of the composition, where the one or more precious metal catalyst is uniformly distributed throughout the at least one cation exchange layer.

[0008] The processes of making such materials are also described in the present invention. In one aspect, the present invention relates to A method of making a solid composition comprising:

- a. melting at least one non-crosslinked fluorinated sulfonyl fluoride polymer;
- b. uniformly distributing at least one precious metal catalyst in the at least one molten non-crosslinked fluorinated sulfonyl fluoride polymer in an amount to form a composition comprising about 90% to about 99.99% by weight of one or more non-crosslinked fluorinated sulfonyl fluoride polymers and about 0.01% to about 10% by weight of one or more precious metal catalysts, based on the total weight of the composition; and
- c. cooling the mixture of step b to form a solid composition.

[0009] In another aspect, the present invention relates to a method of making a cation exchange membrane comprising:

- d. melting at least one non-crosslinked fluorinated sulfonyl fluoride polymer;
- e. uniformly distributing at least one precious metal catalyst with the at least one molten non-crosslinked fluorinated sulfonyl fluoride polymer in an amount to form a composition comprising about 90% to about 99.99% by weight of one or more non-crosslinked fluorinated sulfonyl fluoride polymers and about 0.01% to about 10% by weight of one or more precious metal catalysts, based on the total weight of the composition;
- f. forming a layer of material from the composition of step e, where the precious metal catalyst is uniformly distributed throughout the layer; and
- g. converting the non-crosslinked fluorinated sulfonyl fluoride polymer from the layer of step f to a non-crosslinked fluorinated sulfonic acid polymer. A cathode exchange membrane made by the above method is also envisioned.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] FIG. 1 is a scanning electron micrograph (SEM) image of Example 6.

[0011] FIG. 2 is an SEM image of Example 8.

[0012] FIG. 3 is an SEM image of Example 9.

[0013] FIG. 4 is an SEM image of Example 9 showing the thickness of the precious metal catalyst layer.

[0014] FIG. 5 is an SEM image of Example 17.

[0015] FIG. 6 is an SEM image of Example 18.

[0016] FIG. 7 is an SEM image of Comparative Example A.

DETAILED DESCRIPTION OF THE INVENTION

[0017] Features of the embodiments of the present invention described in the Detailed Description of the Invention can be combined in any manner. All tradenames are designated by capitalization of the brand name.

Definitions

[0018] As used herein, the term uniformly distributed refers to precious metal catalyst being distributed uniformly throughout the volume in all three dimensions. The process of uniformly distributing refers to distributing the material (or rather, redistributing the material) uniformly throughout three dimensions.

[0019] As used herein, the term uniformly dispersed refers to precious metal catalyst being in a de-agglomerated form, such as discrete particles. The process of uniformly dispersing refers to reducing the particle size of the original material by de-agglomerating the original particle into a smaller particle, for example, a primary particle with higher surface area.

[0020] As used herein, the term non-crosslinked fluorinated sulfonyl fluoride polymer refers to fluorinated sulfonyl fluoride polymers having no intentional crosslinkable monomers or repeat units and no added crosslinking agents. The term non-crosslinked fluorinated sulfonic acid refers to fluorinated sulfonic acid polymers having no intentional crosslinkable monomers or repeat units, no added crosslinking agents, and where the sulfonic acid units are not bonded to other polymer units.

[0021] As used herein, ion exchange ratio (IXR) refers to the number of carbon atoms in the polymer backbone in relation to the number of sulfonyl fluoride groups.

[0022] As used herein, a cation exchange membrane precursor refers to a film that is capable of being converted into a cation exchange membrane by hydrolysis and

optional acidification. In this case, the cation exchange membrane precursor is a film comprising a fluorinated sulfonyl fluoride polymer. By the same means, a cation exchange resin precursor is a polymer or resin that is capable of being converted into a cation exchange polymer by hydrolysis and optional acidification.

[0023] The present invention relates to a composition comprising about 90% to about 99.99% by weight of one or more non-crosslinked fluorinated sulfonyl fluoride polymers and about 0.01% to about 10% by weight of one or more precious metal catalyst, based on the total weight of the composition, where the one or more precious metal catalyst is uniformly distributed throughout the one or more non-crosslinked fluorinated sulfonyl fluoride polymer.

[0024] The precious metal catalyst can be any precious metal catalyst typically found in electrolytic cell applications. The precious metal may be, but is not limited to, platinum, ruthenium, osmium, rhodium, iridium, palladium, or mixtures thereof. The precious metal may also be mixed with additional compounds, as long as the precious metal content meets the range of about 0.01-10% by weight of the total composition. The precious metal catalyst may be unsupported, or it may be supported by an inorganic support. Inorganic supports may be in any form, such as an inorganic support particle. Inorganic materials composing the inorganic supports may be any suitable material, including but not limited to, carbon or inorganic materials such as those cited in US20080161429 or EP1929574, which are hereby incorporated by reference; or mixtures thereof. Precious metal catalysts may have a high surface area to increase effectiveness, such that they have a precious metal surface area of at least 10 m²/g; in another aspect, at least 30 m²/g; and in another aspect, at least 45 m²/g. In one aspect, the precious metal catalyst has an average particle size D50 less than about 5 µm; in another aspect, about 75 nm; in another aspect, an average particle size D50 less than about 50 nm; and in another aspect, an average particle size D50 less than about 25 nm.

[0025] Ion exchange membranes can be made of various ion exchange polymers. Preferred ion exchange polymers, fluorinated sulfonic acids and fluorinated sulfonate salts, can be made by hydrolyzing and then optionally protonating fluorinated sulfonyl fluoride polymers. The fluorinated sulfonic acids, fluorinated sulfonate salts, and fluorinated sulfonyl fluoride polymers may or may not be chemically stabilized by fluorinating the polymer endgroups. Suitable fluorinated sulfonyl fluoride polymers

include at least one fluorinated sulfonyl fluoride repeat unit and optionally one or more repeat units, resulting from the free radical polymerization of at least one fluorinated sulfonyl fluoride monomer and optionally one or more monomers. For example, the fluorinated ionomer may contain the repeat unit:



where b is 0 or 1; c is an integer from 1 to 8; a is 0, 1, or 2; d is an integer from 1 to 8; and R_f and R'_f are independently selected from F, Cl or a perfluorinated alkyl group having 1 to 10 carbon atoms. For clarity, it is noted that the segment ((CF₂)_b-(O-(CF₂CFR_f)_c)-O-(CF₂CFR'_f)_dSO₂F) in the structure above is the pendant chain from the perfluorinated polymer backbone. Branched pendant chains having multiple sulfonyl fluoride groups are also encompassed.

[0026] In one aspect, the sulfonyl fluoride polymer is a copolymer made from two or more monomers. In addition to the sulfonyl fluoride monomer, suitable comonomers include, but are not limited to, tetrafluoroethylene (TFE), hexafluoropropylene, vinyl fluoride, vinylidene fluoride, trifluoroethylene, chlorotrifluoroethylene, perfluoro (alkyl vinyl ether), and mixtures thereof. For example, it may be a copolymer of a sulfonyl fluoride-containing monomer with TFE, resulting in a repeat unit $-\text{[CF}_2\text{-CF}_2\text{]-}$, or with other comonomers. Monomers having pendant phosphonic acid groups may also be incorporated into the fluorinated sulfonyl fluoride polymer to yield, after conversion, a fluorinated ionomer containing both sulfonic acid groups and phosphonic acid groups.

[0027] A class of preferred fluorinated sulfonyl fluoride polymers include a highly fluorinated, most preferably perfluorinated, carbon backbone with a side chain represented by the formula $-(\text{O-CF}_2\text{CFR}^f)_a\text{-O-CF}_2\text{CFR}^f\text{SO}_2\text{F}$, where R^f and R'^f are independently selected from F, Cl, or a perfluorinated alkyl group having 1 to 10 carbon atoms and a = 0, 1 or 2. These polymers are converted to sulfonates or sulfonic acids, for example, polymers disclosed in U.S. Patent No. 3,282,875, in U.S. Patent No. 4,358,545, or in U.S. Patent No. 4,940,525.

[0028] One preferred fluorinated sulfonyl fluoride polymer includes a perfluorocarbon backbone and a side chain represented by the formula $-\text{O-CF}_2\text{CF}(\text{CF}_3)\text{-O-CF}_2\text{CF}_2\text{SO}_2\text{F}$. Fluorinated ionomers containing sulfonate or sulfonic acid groups of this type are disclosed in U.S. Patent No. 3,282,875 and may be made by copolymerization of tetrafluoroethylene (TFE) and the perfluorinated vinyl

ether $\text{CF}_2=\text{CF}-\text{O}-\text{CF}_2\text{CF}(\text{CF}_3)-\text{O}-\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$, perfluoro(3,6 dioxo-4 methyl 7 octenesulfonyl fluoride) (PSEPVE, also called long side-chain or LSC), followed by conversion to sulfonate groups by hydrolysis of the sulfonyl fluoride groups and conversion to the proton form if desired for the particular application. Another preferred fluorinated sulfonyl fluoride polymer is of the type disclosed in U.S. Patent No. 4,358,545 and U.S. Patent No. 4,940,525, which has the side chain $-\text{O}-\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$. This polymer may be made by copolymerization of TFE and the perfluorinated vinyl ether $\text{CF}_2=\text{CF}-\text{O}-\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$, perfluoro(3 oxa-4-pentenesulfonyl fluoride) (PFSVE, also called short side-chain or SSC), followed by hydrolysis and conversion to the proton form if desired for the particular application.

[0029] After hydrolysis and optional conversion to the proton form, a fluorinated sulfonate or sulfonic acid polymer is formed. As used herein, sulfonate or sulfonic acid groups refers to either sulfonic acid groups or salts of sulfonic acid, preferably alkali metal or ammonium salts. Preferred functional groups are represented by the formula $-\text{SO}_3\text{X}$ wherein X is H, Li, Na, K or $\text{N}(\text{R}^1)(\text{R}^2)(\text{R}^3)(\text{R}^4)$, where R^1 , R^2 , R^3 , and R^4 are the same or different and are H, CH_3 , or C_2H_5 . In exemplary embodiments, the fluorinated sulfonate or sulfonic acid polymer is of the type available under the trade name of Nafion™ (The Chemours Company FC, LLC, Wilmington, DE).

[0030] For example, the fluorinated ionomer may contain the repeat unit:



where b is 0 or 1; c is an integer from 1 to 8; a is 0, 1, or 2; d is an integer from 1 to 8; R_f and R'_f are independently selected from F, Cl or a perfluorinated alkyl group having 1 to 10 carbon atoms; and X is H, Li, Na, K or $\text{N}(\text{R}^1)(\text{R}^2)(\text{R}^3)(\text{R}^4)$ where R^1 , R^2 , R^3 , and R^4 are the same or different and are H, CH_3 or C_2H_5 . For clarity, it is noted that the segment $((\text{CF}_2)_b-\text{O}-(\text{CF}_2\text{CFR}_f)_c-\text{O}-(\text{CF}_2\text{CFR}'_f)_d\text{SO}_3\text{X})$ in the structure above is the pendant chain from the perfluorinated polymer backbone. Branched pendant chains having multiple sulfonic acid groups are also encompassed.

[0031] In some embodiments, the fluorinated sulfonyl fluoride polymer has an ion exchange ratio of less than about 13.2. As used herein, ion exchange ratio (IXR) refers to the number of carbon atoms in the polymer backbone in relation to the number of sulfonyl fluoride groups. In some embodiments, the IXR of a fluorinated sulfonyl fluoride polymer can be related to the equivalent weight (EW) of the corresponding fluorinated sulfonate or sulfonic acid polymer by the equation $\text{EW} =$

$(50 \times \text{IXR}) + \text{MW}_{\text{sc}} - 19$, where MW_{sc} is the molecular weight of the side chain of the fluorinated sulfonate or sulfonic acid polymer. In one aspect, the fluorinated sulfonyl fluoride polymer has an IXR less than about 13.2; in another aspect, less than about 12.7; in another aspect, less than about 12.1; and in another aspect, less than about 11.7; or any value, range, or sub-range therebetween. In one aspect, the fluorinated sulfonyl fluoride polymer has an IXR of at least 7.1; in another aspect, at least 8.1; in another aspect, at least 9.1; and in another aspect, at least 10.1; or any value, range, or sub-range therebetween.

[0032] In some embodiments, the fluorinated sulfonyl fluoride polymer and corresponding fluorinated sulfonate or sulfonic acid polymer has an equivalent weight (EW) less than about 1000; alternatively, less than about 980; alternatively less than about 950; alternatively less than about 930, or any value, range, or sub-range therebetween. In one aspect, the corresponding fluorinated sulfonate or sulfonic acid polymer has an EW of at least about 530; alternatively, at least about 580; alternatively, at least about 630; alternatively at least about 680, or any value, range, or sub-range therebetween. As used herein, (EW) refers to the weight of the corresponding fluorinated sulfonic acid polymer in proton form required to neutralize one equivalent of NaOH.

[0033] In one aspect, the fluorinated sulfonyl fluoride polymer and its corresponding fluorinated sulfonate or sulfonic acid polymer contains the long side chain and has an EW less than about 1000; alternatively less than about 980; alternatively less than about 950; alternatively less than about 930, or any value, range, or sub-range therebetween. In one aspect, the fluorinated sulfonyl fluoride polymer and its corresponding fluorinated sulfonate or sulfonic acid polymer has an EW of at least about 700; alternatively, at least about 750; alternatively, at least about 800; alternatively at least about 950, or any value, range, or sub-range therebetween. The IXR for a fluorinated polymer with the side chain $-\text{O}-\text{CF}_2-\text{CF}(\text{CF}_3)-\text{O}-\text{CF}_2-\text{CF}_2-\text{SO}_3\text{H}$, i.e., produced from a copolymer of TFE and PSEPVE, can be related to EW using the following formula: $50 \text{ IXR} + 344 = \text{EW}$.

[0034] In another embodiment, the fluorinated sulfonyl fluoride polymer and its corresponding fluorinated sulfonate or sulfonic acid polymer contains the short side chain and has an EW less than about 840; alternatively less than about 810; alternatively less than about 785; alternatively less than about 765, or any value,

range, or sub-range therebetween. In one aspect, the fluorinated sulfonyl fluoride polymer and its corresponding fluorinated sulfonate or sulfonic acid polymer has an EW of at least about 530; alternatively, at least about 580; alternatively, at least about 630; alternatively at least about 680, or any value, range, or sub-range therebetween. The IXR for a fluorinated polymer with the side chain -O-CF₂CF₂SO₃H, i.e., produced from a copolymer of TFE and PFSVE, can be related to equivalent weight using the following formula: $50 \text{ IXR} + 178 = \text{EW}$.

[0035] In this invention, the precious metal catalyst is specifically combined with the fluorinated sulfonyl fluoride version of the polymer, rather than the corresponding fluorinated sulfonate or fluorinated sulfonic acid. It is believed that blending the precious metal catalyst directly into the fluorinated sulfonyl fluoride will allow more uniformly distributed and more uniformly dispersed catalyst throughout the polymer, leading to a more uniformly distributed or more uniformly dispersed catalyst in materials made from the composition, such as fluorinated sulfonyl fluoride films, corresponding fluorinated sulfonate polymer materials, corresponding fluorinated sulfonic acid polymer materials, and films or membranes thereof. In one aspect, the precious metal catalyst is uniformly dispersed throughout the composition.

[0036] The precious metal catalyst is present in the composition in an amount sufficient to provide gas recombination effects, but not so much as to alter the electrical conductivity (or lack thereof) of the non-crosslinked fluorinated sulfonyl fluoride polymer, or of its corresponding fluorinated sulfonate polymer or fluorinated sulfonic acid polymer. In one aspect, the composition comprises about 90% to about 99.99% by weight of one or more non-crosslinked fluorinated sulfonyl fluoride polymers and about 0.01% to about 10% by weight of one or more precious metal catalyst, based on the total weight of the composition. In another aspect, the composition comprises about 92% to about 99.9% by weight of one or more non-crosslinked fluorinated sulfonyl fluoride polymers and about 0.1% to about 8% by weight of one or more precious metal catalyst; in another aspect, about 95% to about 99.7% by weight of one or more non-crosslinked fluorinated sulfonyl fluoride polymers and about 0.3% to about 5% by weight of one or more precious metal catalyst; about 97% to about 99.5% by weight of one or more non-crosslinked fluorinated sulfonyl fluoride polymers and about 0.5% to about 3% by weight of one or more precious metal catalyst; about 98% to about 99.3% by weight of one or more

non-crosslinked fluorinated sulfonyl fluoride polymers and about 0.7% to about 2% by weight of one or more precious metal catalyst; about 98.5% to about 99.3% by weight of one or more non-crosslinked fluorinated sulfonyl fluoride polymers and about 0.7% to about 1.5% by weight of one or more precious metal catalyst; or any value, range, or sub-range therebetween; all based on total weight of the composition.

[0037] Additional compounds may be present in the composition, but preferably, the composition comprises less than about 5% by weight of any additional compounds, based on the total composition weight. In another aspect, the composition comprises less than about 3% by weight of additional compounds; in another aspect, the composition comprises less than about 2% by weight of additional compounds; in another aspect, the composition comprises less than about 1% by weight of additional compounds; in another aspect, the composition comprises less than about 0.5% of additional compounds; or any value, range, or sub-range therebetween; all based on total weight of the composition. Suitable additional compounds include, but are not limited to, radical scavenger compounds, coupling agents, or other resin additives.

[0038] In one aspect, the composition contains less than 5% by weight of solvent or liquid carrier; in another aspect, less than 2% by weight of solvent or liquid carrier; in another aspect, less than 1% by weight of solvent or liquid carrier; in another aspect, less than 0.1% by weight of solvent or liquid carrier; and in another aspect, 0% solvent or liquid carrier; or any value, range, or sub-range therebetween; all based on total weight of the composition. In one aspect, no solvent or liquid carrier is present in the composition, such that the total weight of the composition is the equal to the total dry weight of the composition.

[0039] The composition can be a solid composition and can be made by a method comprising:

- a. melting at least one non-crosslinked fluorinated sulfonyl fluoride polymer;
- b. uniformly distributing at least one precious metal catalyst in the at least one molten non-crosslinked fluorinated sulfonyl fluoride polymer in an amount to form a composition comprising about 90% to about 99.99% by weight of one or more non-crosslinked fluorinated sulfonyl fluoride polymers and about 0.01% to about 10% by

weight of one or more precious metal catalysts, based on the total weight of the composition; and

c. cooling the mixture of step b to form a solid composition.

[0040] In this method, the precious metal catalyst is combined with the non-crosslinked fluorinated sulfonyl fluoride polymer in the melt. Suitable precious metal catalysts, non-crosslinked fluorinated sulfonyl fluoride polymers, composition, and component amounts are the same as those listed above. Suitable temperatures for steps a and b can be envisioned by one of skill in the art but include temperatures above the melting point of the non-crosslinked fluorinated sulfonyl fluoride polymer where the temperature produces a polymer with a viscosity of suitable level to allow for extrusion.

[0041] The precious metal catalyst is uniformly distributed in the non-crosslinked fluorinated sulfonyl fluoride polymer, and in one aspect, the precious metal catalyst is uniformly dispersed throughout the non-crosslinked fluorinated sulfonyl fluoride polymer in step b. Uniform distribution step b can occur by any mixing method suitable to distribute or disperse the precious metal catalyst in the resin, such as any mixing method that exerts high mixing and/or shear to the components. These methods include but not limited to mixing in a single-screw extruder or mixing in a twin-screw extruder, where screw elements such as a knead block or gear mixer may also be included. In one aspect, the process further comprises a step of mixing solid non-crosslinked fluorinated sulfonyl fluoride with solid precious metal catalyst prior to melting step a, such that the non-crosslinked fluorinated sulfonyl fluoride polymer is melted in step a with the precious metal catalyst already present. However, other methods of introducing the precious metal catalyst to the composition may also be used, including but not limited to feeding the precious metal catalyst into the molten non-crosslinked fluorinated sulfonyl fluoride polymer in the mixing apparatus.

[0042] It is desired to have the precious metal catalyst highly dispersed within that layer of the membrane to prevent it from agglomerating. In one aspect, a low surface energy molten polymer resin is mixed with a high surface energy filler, operating at a high temperature to reduce the polymer viscosity, and with high shear forces. By operating under those conditions, one should obtain a well dispersed (highly active) precious metal catalyst within a cation exchange membrane layer.

Following step b, the precious metal catalyst may have an average particle size D50 less than about 5 μm ; in another aspect, about 75 nm; in another aspect, an average particle size D50 less than about 50 nm; and in another aspect, an average particle size D50 less than about 25 nm.

[0043] To form a solid composition, the mixture of step b is cooled by any suitable method of reducing temperature. For example, the mixture may simply be cooled by removing heat, such as after removing from the heating vessel. Active cooling methods may also be applied to speed the solidification process. In one aspect, the process further comprises a step of shaping the mixture of step b prior to cooling. For example, the mixture of step b may be extruded, pelletized, and cooled. In another aspect, the mixture of step b may be extruded, melt cast, or poured into a film and cooled. Without being bound to one specific theory, it is believed that the act of cooling or quenching the polymer resin mixture after mixing serves to lock the precious metal catalyst compounds in place to prevent agglomeration and sedimentation, which is a specific difficulty obtained from the current state of the art using a GRC mixed into a PFSA dispersion where the metal catalyst particles are known to settle over time.

[0044] Another aspect of the current invention relates to a cation exchange membrane precursor comprising at least one cation exchange precursor layer, where the at least one proton exchange precursor layer comprises about 90% to about 99.99% by weight of one or more non-crosslinked fluorinated sulfonyl fluoride polymers and about 0.01% to about 10% by weight of one or more precious metal catalysts, based on the total weight of the composition, where the one or more precious metal catalyst is uniformly distributed throughout the at least one proton exchange precursor layer. Suitable precious metal catalysts, non-crosslinked fluorinated sulfonyl fluoride polymers, composition components, and component amounts are the same as those listed above.

[0045] The cation exchange membrane precursor may include at least one additional layer; in another aspect, the cation exchange membrane precursor includes at least two additional layers, where two layers are represented by the terms additional layer and third layer; and in another aspect, the cation exchange membrane precursor includes at least three additional layers, where three layers are represented by the terms additional layer, third layer, and fourth layer. The additional

layers may contain an ion exchange resin precursor, such as but not limited to, fluorinated sulfonyl fluoride polymer. Such ion exchange resin precursors may be crosslinkable, crosslinked, or non-crosslinked. In one aspect, the ion exchange resin precursors fall within the IXR or EW ranges described above. The additional layers may be present in the same film as the original cation exchange precursor layer, or they may be one or more separate films that are later joined to form the cation exchange membrane.

[0046] The at least one additional layers may also independently contain additives, including radical scavengers, precious metal catalysts, other additives, or mixtures thereof. In one aspect, the radical scavengers, precious metal catalysts, and other additives are present in the additional layers in the amounts described above. The composition of the additional layers may be the same or different as the first cation exchange precursor layer, and they also may be the same or different than each other. In one aspect, the additional layer does not contain precious metal catalyst. In one aspect, there are three additional layers, where two of the additional layers do not contain precious metal catalyst; and in another aspect, there are three additional layers, where the total four layer structure has alternating layers of layers containing precious metal catalyst and layers that do not contain precious metal catalyst.

[0047] It is thought that GRC is most active in certain locations of the membrane, either closer to the anode or cathode depending on the cell operation. Therefore, in one aspect of the invention, there are precious metal catalyst loadings in specific locations of the membrane closest to the anode or cathode, while having no precious metal catalyst in other locations.

[0048] In one aspect of the invention, the cation exchange membrane precursor is unreinforced. However, in another aspect of the invention, a reinforcement layer is present to provide additional mechanical strength to the overall membrane precursor structure. Reinforcement layers can be any material suitable for providing this additional mechanical strength while also allowing cations to move freely through the structure. For example, the reinforcement may be a porous film, woven fabric, or porous scrim material, composed of materials including but not limited to polytetrafluoroethylene (PTFE), polyaryl ether ketone (PAEK), liquid crystal polymer, polyphenylene sulfide (PPS), PTFE-perfluoroalkyl vinyl ether copolymer (PFA), glass, quartz, and polyolefins including polyethylene or polypropylene. Specific PTFE

reinforcements include porous expanded PTFE (ePTFE) and woven PTFE.

Examples of materials having a high tensile modulus that are suitable as reinforcement materials include liquid crystal polymer, polyphenylene sulfide, glass, quartz, or PAEK. Specific polyaryl ether ketones include, but are not limited to, polyether ketone (PEK), polyether ether ketone (PEEK), polyether ketone ketone (PEKK), polyether ether ketone ketone (PEEKK), or polyether ketone ether ketone ketone (PEKEKK).

[0049] In one aspect, the final cation exchange membrane precursor may have an average thickness of about 25-150 μm ; in another aspect, an average thickness of about 30-120 μm ; in another aspect, an average thickness of about 30-100 μm ; in another aspect, an average thickness of about 30-80 μm ; and in another aspect, an average thickness of about 30-60 μm . Lower thicknesses may be desirable to target high efficiency, while higher thicknesses may be desirable to target high durability. It may be desirable to have a specific layer of GRC within the membrane where the highest concentration of hydrogen and oxygen are present to increase the efficiency of the GRC material while minimizing the amount of GRC material that is needed. In one aspect, the layer within the membrane having precious metal catalyst may have a thickness of about 3 μm to about 150 μm ; in another aspect, about 7 μm to about 150 μm ; and in another aspect, about 17 to about 150 μm . When other cation exchange layers are present in the membrane, the layer within the membrane having precious metal catalyst may have a thickness of about 3 μm to about 100 μm ; in another aspect, about 7 μm to about 50 μm ; and in another aspect, about 17 to about 25 μm .

[0050] It follows that the invention also relates to cation exchange membranes comprising at least one cation exchange layer, where the at least one cation exchange layer comprises about 90% to about 99.99% by weight of one or more non-crosslinked fluorinated sulfonic acid polymers or non-crosslinked fluorinated sulfonate polymers and about 0.01% to about 10% by weight of one or more precious metal catalysts, based on the total weight of the composition, where the one or more precious metal catalyst is uniformly distributed throughout the at least one cation exchange layer. In one aspect, the one or more precious metal catalyst is uniformly distributed. The cation exchange membranes are made by hydrolyzing and optionally protonating the cation exchange membrane precursor, where the non-

crosslinked fluorinated sulfonyl fluoride polymers as described above are converted to non-crosslinked fluorinated sulfonate polymers or non-crosslinked fluorinated sulfonic acid polymers. Suitable precious metal catalysts, non-crosslinked fluorinated sulfonyl fluoride polymers and their corresponding non-crosslinked fluorinated sulfonates and sulfonic acids, composition, component amounts, and layer structures are the same as those listed above.

[0051] The cation exchange membranes may also have one or more additional layers, as described above. In this case, the one or more additional layers may comprise a cation exchange resin rather than a ion exchange precursor, including but not limited to a fluorinated sulfonate polymer or fluorinated sulfonic acid polymer. Such ion exchange resins may be crosslinkable, crosslinked, or non-crosslinked. In one aspect, the cation exchange resin fall within the IXR or EW ranges described above. The additional layers may be present in the same film as the original cation exchange layer, or they may be one or more separate films that are later joined to form the cation exchange membrane. As stated for the cation exchange membrane precursor, the cation exchange membrane may be unreinforced. However, in another aspect of the invention, a reinforcement layer is present to provide additional mechanical strength to the overall membrane precursor structure. Reinforcement layers can be any material suitable for providing this additional mechanical strength while also allowing cations to move freely through the structure. Suitable reinforcement materials are described above.

[0052] The cation exchange membranes can be made by a method comprising:

- d. melting at least one non-crosslinked fluorinated sulfonyl fluoride polymer;
- e. uniformly distributing at least one precious metal catalyst with the at least one molten non-crosslinked fluorinated sulfonyl fluoride polymer in an amount to form a composition comprising about 90% to about 99.99% by weight of one or more non-crosslinked fluorinated sulfonyl fluoride polymers and about 0.01% to about 10% by weight of one or more precious metal catalysts, based on the total weight of the composition;
- f. forming a layer of material from the composition of step e, where the precious metal catalyst is uniformly distributed throughout the layer; and
- g. converting the non-crosslinked fluorinated sulfonyl fluoride polymer from the layer of step f to a non-crosslinked fluorinated sulfonic acid polymer or non-crosslinked

fluorinated sulfonate polymer. A cathode exchange membrane made by the above method is also envisioned. The cation exchange membrane precursor results from the process above, stopping before the conversion step g. Suitable precious metal catalysts, non-crosslinked fluorinated sulfonyl fluoride polymers and their corresponding non-crosslinked fluorinated sulfonates and sulfonic acids, composition, component amounts, and layer structures are the same as those listed above.

[0053] As noted above for the solid composition process, suitable temperatures for steps d and e can be envisioned by one of skill in the art but include temperatures above the melting point of the non-crosslinked fluorinated sulfonyl fluoride polymer where the temperature produces a polymer with a viscosity of suitable level to allow for extrusion. The precious metal catalyst is uniformly distributed in the non-crosslinked fluorinated sulfonyl fluoride polymer, and in one aspect, the precious metal catalyst is uniformly dispersed throughout the non-crosslinked fluorinated sulfonyl fluoride polymer in step e. Uniform distribution step e can occur by any mixing method suitable to distribute or disperse the precious metal catalyst in the resin, such as any mixing method that exerts high mixing and/or shear to the components. These methods include but not limited to mixing in a single-screw extruder or mixing in a twin-screw extruder, where screw elements such as a knead block or gear mixer may also be included. In one aspect, the process further comprises a step of mixing solid non-crosslinked fluorinated sulfonyl fluoride with solid precious metal catalyst prior to melting step d, such that the non-crosslinked fluorinated sulfonyl fluoride polymer is melted in step d with the precious metal catalyst already present. However, other methods of introducing the precious metal catalyst to the composition may also be used, including but not limited to feeding the precious metal catalyst into the molten non-crosslinked fluorinated sulfonyl fluoride polymer in the mixing apparatus.

[0054] In one aspect, the composition of step e is cooled prior to forming a layer of material in step f. In another aspect, the method further comprises step e1 of shaping and cooling the composition of step e before step f. The mixture of step e is cooled by any suitable method of reducing temperature. For example, the mixture may simply be cool by removing heat, such as after removing from the heating vessel. Active cooling methods may also be applied to speed the solidification

process. In one aspect, the process further comprises a step of shaping the mixture of step e prior to cooling. For example, the mixture of step e may be extruded, pelletized, cooled, and remelted prior to step f. In another aspect, the mixture of step e may be extruded or poured directly into a film and cooled.

[0055] In step f, the formation of a layer of composition, the formation may occur by any suitable means, including extrusion, melt casting, pouring, or pressing a solid composition at elevated temperature. In one aspect, the composition of step e is extruded into a film during step f. Extrusion may be performed using a single-screw extruder or twin-screw extruder, where screw elements such as a knead block or gear mixer may also be included, before extrusion into a film shape.

[0056] The additional layers may be formed by any suitable means, including extrusion, pouring, or pressing a solid composition at elevated temperature. The additional layers may be combined with the layer of material from step f by any suitable process, including co-extrusion or lamination. In one aspect, the at least one additional layer is formed by coextruding with the layer of step f to form a single film. Such a coextrusion could occur, for example, by providing separate feedstock for the layer of step f and the at least one additional layer, and then joining the feedstocks during extrusion. In another aspect, the at least one additional layer is separately formed and pressed together at elevated temperature with a film having a layer of step f.

[0057] As described above, reinforcement layers may be used in the cation exchange membrane precursors and cation exchange membranes. When a reinforcement is used, the process includes applying the composition of step e to a reinforcement material either during the layer formation step f or after layer formation step f. When the composition of step e is applied to the reinforcement during the layer formation step f, it may be extruded and melt laminated onto the reinforcement by any suitable process, including but not limited to extrusion lamination. In another aspect, when the composition of step e is applied to the reinforcement after layer formation step f, it may be laminated by any suitable process, such as but not limited to by double belt lamination, nip roll lamination, vacuum lamination. The extruded film can then be laminated at elevated temperature with the woven reinforcement to fuse the polymer and woven layer together into a composite film according to typical

lamination methods, such as by using a lamination roll or a vacuum lamination process.

[0058] The non-crosslinked fluorinated sulfonyl fluoride of the layer of step f may then be converted in step g to a non-crosslinked fluorinated sulfonate or non-crosslinked fluorinated sulfonic acid. Any convertible polymers from additional layers may be converted simultaneously as part of the same film, a composite film. The film or composite film may be hydrolyzed in an aqueous alkali metal hydroxide solution and acidified by acid, such as nitric acid, to convert the sulfonyl fluoride groups to sulfonic acid or sulfonate groups. Alkali metal hydroxides include but are not limited to NaOH or KOH. During the hydrolysis step, a water-soluble organic solvent may be employed in the hydrolysis solution, such as dimethyl sulfoxide (DMSO), N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidinone, N-ethyl-2-pyrrolidone, methanol, ethanol, isopropanol, butanol, methoxyethoxyethanol, butoxyethanol, butylcarbitol, hexyloxyethanol, octanol, propylene glycol methyl ether, ethylene glycol, ethanolamine, N-methylethanolamine, N-ethylethanolamine, 1-amino-2-propanol, 1-amino-3-propanol, 2-aminoethoxyethanol, 2-aminoethoxyethanol, and 2-amino-2-methyl-1-propanol.

[0059] In one aspect, the final reinforced ion exchange membranes may have an average thickness of about 30-150 μm ; in another aspect, an average thickness of about 30-120 μm ; in another aspect, an average thickness of about 30-100 μm ; in another aspect, an average thickness of about 30-80 μm ; and in another aspect, an average thickness of about 30-60 μm .

[0060] The cation exchange membranes may be used in catalyst coated membranes, having multiple layers of functional materials. Such catalyst coated membranes may be used in electrolytical systems, for example, a water electrolysis system. In one aspect, the invention relates to a catalyst coated membrane comprising the cation exchange membrane, where the catalyst coated membrane comprises a cathode catalyst layer on one side of the reinforced ion exchange membrane and an anode catalyst layer on another side of the reinforced ion exchange membrane. A catalyst coated membrane may comprise a cathode catalyst layer (CCL) on one side of the ion exchange membrane and an anode catalyst layer (ACL) on another side of the ion exchange membrane. For example, a cathode catalyst layer may be in direct contact with a cation exchange membrane, and the

cation exchange membrane may be in further direct contact with anode catalyst layer to make catalyst coated membrane. The cation exchange membrane may comprise multiple layers and may also including a reinforcement layer. The catalyst coated membrane may contain multiple layers of the same material, and it may contain additional layers of functional materials, such as gas diffusion layers, porous transport layers, or bipolar plates.

[0061] The CCL and ACL may be applied to the ion exchange membrane in the form of a catalyst ink. Catalyst ink compositions often include a catalyst component and a polymer binder, where the polymer binder often includes fluorinated ionomers such as those described above. The polymer used in the CCL and ACL may be the same or different from the polymer used as the fluorinated ionomer of the ion exchange membrane. Catalyst components may include but are not limited to metal particles or carbon-supported metal particles. Specific metals may include but are not limited to platinum, ruthenium, gold, silver, palladium, iridium, rhodium, iron, cobalt, nickel, chromium, tungsten, manganese, vanadium, and alloys thereof. Solvents, such as those mentioned for use in the ion exchange dispersion, may be used to aid in application of the catalyst ink to the ion exchange membrane. The CCL and ACL materials may be applied to the ion exchange membrane by any suitable means, including brushing, spraying, notch bar coating, fluid die coating, rod coating, slot-fed knife coating, three-roll coating, or decal transfer.

EXAMPLES

[0062] The following test methods and materials were used in the examples herein.

[0063] The invention is illustrated in the following examples which do not limit the scope of the invention as described in the claims. The following test methods and materials were used in the examples herein.

[0064] All solvents and reagents, unless otherwise indicated, are available from Sigma-Aldrich, St. Louis, MO.

[0065] HSAPB was High Surface Area Platinum Black having a Pt crystallite size of 5.0-7.5 nm, Pt surface area ECSA of 50 m²/g, and total catalyst surface area of 50 m²/g; all available from The Fuel Cell Store, College Station, TX. Platinum Black TA

HSTDP was a platinum black product having a BET Pt surface area of 27 m²/g, available from Heraeus Precious Metals, Santa Fe Springs, CA.

[0066] Catalyst ink component IrO₂ was available from Alpha Aesar Premion®, Ward Hill, MA, and catalyst ink component Pt/C was TKK TEC10E50E, available from Tanaka Precious Metals, Tokyo, Japan.

[0067] The TiO₂-supported Pt catalyst was available from Ishifuku Metal Industry Company, Tokyo, Japan.

[0068] Platinum on carbon catalyst TEC10V50E had a Pt content of 46.8% by weight, a particle size of 23 Å as measured by XRD, and a BET Pt surface area of 106.8 m²/g, available from TKK, Tokyo, Japan.

[0069] Nafion™ D2020 is an ionomer dispersion available from The Chemours Company, Wilmington, DE.

[0070] The PEEK reinforcing fabric used was IEM 17-195/70, a plain weave fabric having fibers of approximately 38 µm in diameter, a center-to-center fiber spacing of about 195 µm, open area of about 70%, available from SEFAR, Thal, Switzerland.

TEST METHODS

Thickness

[0071] Three thickness measurements were taken with a ProGage thickness measurement gauge available from Thwing-Albert Instrument Company, West Berlin, NJ. The reported thickness represents an average of the three measurements.

Hydrogen/Oxygen Crossover

[0072] A catalyst coated membrane was made by spraying a catalyst ink onto the formed membranes, which were affixed to a vacuum plate heated to 80 °C. The anode catalyst ink contained 0.4 mg/cm² of IrO₂ and Nafion™ D2020 (weight ratio of 0.84:0.16), and the cathode catalyst ink contained 0.1 mg/cm² of Pt/C and Nafion™ D2020 (weight ratio 0.15:0.85).

[0073] The H₂:O₂ ratio in the anode exhaust stream of the cell was quantified using Gas Chromatography (GC). At the cell outlet, the mixture contained liquid water, oxygen, hydrogen, and water vapor. N₂ gas was also added to ensure that the mixture remained below the flammability limit. The mixture was routed through a series of components designed to condense and remove liquid water to protect the

GC. Samples were taken continuously until the H₂:O₂ ratio equilibrated, typically between 5-15 minutes.

SEM Image of Compounded Resin and Membrane

[0074] Samples were sputter coated with osmium to help minimize charging effects in the electron microscope and then analyzed using backscatter mode on a Auriga 60 CrossBeam SEM. Cross-sections of the membrane were prepared using a microtome.

Example 1

[0075] Into a 1-gallon polyethylene container was mixed 6.0 kg of a 920 equivalent weight sulfonyl fluoride fluoropolymer resin pellets (chemically stabilized PTFE / CF₂=CF-O-CF₂CF(CF₃)-O-CF₂CF₂SO₂F copolymers having an EW of 920 g/mol, available from The Chemours Company, Wilmington, DE). To these pellets was added 60 g of HSAPB. This mixture was roll tumbled for 10 minutes at room temperature to coat the fluoropolymer resin pellets with the platinum. The platinum coated sulfonyl fluoride containing fluoropolymer resin pellets were then fed using a loss-in-weight feeder to a 1" diameter twin screw extruder at a polymer feed rate of 2.27 kg/hour and with a screw speed of 150 RPM. The twin screw extruder contained knead block screw elements to help with distributive mixing of the platinum within the fluoropolymer melt. The temperature profile was from 190 °C in the feed throat and increased to 230 °C at the discharge end. Pellets were strand cut to create black pellets containing 1 wt% platinum.

Example 2

[0076] A multi-layer film was prepared using a co-extrusion system. The first extruder with a 1.5" single-screw was fed with non-platinized sulfonyl fluoride fluoropolymer resin (chemically stabilized PTFE / CF₂=CF-O-CF₂CF(CF₃)-O-CF₂CF₂SO₂F copolymers having an EW of 920 g/mol, available from The Chemours Company, Wilmington, DE) pellets to a feed block. A satellite extruder with a 1" single-screw was fed with the platinized sulfonyl fluoride containing fluoropolymer resin pellets from Example 1. The feed block combined the flows from these two extruders into discreet layers and fed through a die to create a final film with discreet layers of platinized sulfonyl fluoride resin and virgin non-platinized sulfonyl fluoride fluoropolymer resin. The extruders were run at 275 °C and melt cast from a 10 mil die and stretched in the machine direction to a 2 mil final thickness. The films were

hydrolyzed in a solution of DMSO / KOH / water as is taught in the art. The films were then acidified in a solution of 20% nitric acid in water before being dried to remove excess water.

Example 3

[0077] The pre-hydrolyzed film of Example 2 was melt laminated with a PEEK reinforcing fabric to form a composite film. The laminated films were hydrolyzed in a solution of DMSO / KOH / water as is taught in the art. The PEEK reinforcing fabric used was a plain weave fabric having fibers of approximately 38 μm in diameter, a center-to-center fiber spacing of about 195 μm , open area of about 70%. The films were then acidified in a solution of 20% nitric acid in water before being dried to remove excess water.

Example 4

[0078] Example 1 was repeated, except using a screw speed of 300 RPM.

Example 5

[0079] A co-extrusion system was employed where the first extruder with a 2.5" single-screw was fed with non-platinized sulfonyl fluoride containing fluoropolymer resin pellets (chemically stabilized PTFE / $\text{CF}_2=\text{CF}-\text{O}-\text{CF}_2\text{CF}(\text{CF}_3)-\text{O}-\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$ copolymers having an EW of 920 g/mol, available from The Chemours Company, Wilmington, DE) to a feed block. The satellite extruder with a 1.5" single-screw was fed with platinized sulfonyl fluoride containing fluoropolymer resin pellets from Example 4. The feed block combined the flows from these two extruders into discreet layers and feeds through a die to create a final film with discreet layers of platinized sulfonyl fluoride resin and virgin non-platinized sulfonyl fluoride fluoropolymer resin. The extruders were run at 270 °C and melt cast from a 33 mil die and stretched in the machine direction to a 2.3 mil final thickness. The films were hydrolyzed in a solution of DMSO / KOH / water as is taught in the art. The films were then acidified in a solution of 20% nitric acid in water before being dried to remove excess water.

Example 6

[0080] Example 3 was repeated, using the pre-hydrolyzed film of Example 5, and the resulting membrane was tested for $\text{H}_2:\text{O}_2$ Crossover.

Table 1. H₂:O₂ Crossover Performance (%) for Example 6

Current Density (A/cm ²)	Hold Time (hours)					
	0	81	170	236	324	392
0.1	0.41	0.67	0.69	0.70	0.70	0.81
0.25	0.22	0.34	0.35	0.35	0.35	0.40
0.5	0.14	0.20	0.21	0.21	0.22	0.24
1	0.09	0.12	0.13	0.13	0.14	0.15
2	0.07	0.08	0.09	0.10	0.10	0.11

[0081] As can be seen in Table 1, low crossover values are maintained over many hours for the inventive sample, indicating good initial performance and performance durability.

Example 7

[0082] Two separate 1-gallon polyethylene containers were charged with 4.5 kg each of a 920 equivalent weight sulfonyl fluoride fluoropolymer resin pellets (non-chemically stabilized PTFE / CF₂=CF-O-CF₂CF(CF₃)-O-CF₂CF₂SO₂F copolymers having an EW of 920 g/mol, available from The Chemours Company, Wilmington, DE). HSAPB (90 g) was added to one container. This mixture was roll tumbled for 10 minutes at room temperature to coat the fluoropolymer resin pellets with the platinum. The platinum coated sulfonyl fluoride containing fluoropolymer resin pellets were then fed using a loss-in-weight feeder to a 27 mm diameter twin screw extruder at a polymer feed rate of 9.07 kg/hour and with a screw speed of 200 RPM. The twin screw extruder contained knead block screw elements to help with distributive mixing of the platinum within the fluoropolymer melt. The temperature profile was from 160 °C in the feed throat and increased to 190 °C at the discharge end. Pellets were strand cut to create black pellets containing 2 wt% platinum.

Example 8

[0083] Example 5 was repeated, except the fluoropolymer resin pellets of Example 7 were used in place of the resin pellets from Example 4.

Example 9

[0084] Example 3 was repeated, using the pre-hydrolyzed film of Example 8. The resulting membrane was tested for H₂:O₂ Crossover.

Example 10

[0085] Example 7 was repeated, except 45 g of TiO₂-supported Pt was used, yielding pellets containing 1 wt% Pt/TiO₂.

Example 11

[0086] Example 5 was repeated, except the fluoropolymer resin pellets of Example 10 were used in place of the resin pellets from Example 4.

Example 12

[0087] Example 3 was repeated, using the pre-hydrolyzed film of Example 11.

Example 13

[0088] Two separate 1-gallon polyethylene containers were charged with 5 kg each of a 920 equivalent weight sulfonyl fluoride fluoropolymer resin pellets (chemically stabilized PTFE / CF₂=CF-O-CF₂CF(CF₃)-O-CF₂CF₂SO₂F copolymers having an EW of 920 g/mol, available from The Chemours Company, Wilmington, DE). Platinum Black TA HSTDP (72.5 g) was added to one container. This mixture was roll tumbled for 10 minutes at room temperature to coat the fluoropolymer resin pellets with the platinum. The platinum coated sulfonyl fluoride containing fluoropolymer resin pellets were then fed using a loss-in-weight feeder to a 31 mm diameter twin screw extruder at a polymer feed rate of 9.07 kg/hour and with a screw speed of 200 RPM. The twin screw extruder contained knead block screw elements to help with distributive mixing of the platinum within the fluoropolymer melt. The temperature profile was from 160 °C in the feed throat and increased to 190 °C at the discharge end. Pellets were strand cut to create black pellets containing 1.45 wt% platinum.

Example 14

[0089] Example 5 was repeated, except the fluoropolymer resin pellets of Example 13 were used in place of the resin pellets from Example 4.

Example 15

[0090] Example 3 was repeated, using the pre-hydrolyzed film of Example 14. The resulting membrane was tested for H₂:O₂ crossover.

Example 16

[0091] Example 13 was repeated, except 130.5 g of Pt on carbon catalyst TEC10V50E with 9 kg of polymer (chemically stabilized PTFE / CF₂=CF-O-

CF₂CF(CF₃)-O-CF₂CF₂SO₂F copolymers having an EW of 920 g/mol, available from The Chemours Company, Wilmington, DE) was used in place of the platinum black, yielding pellets containing 1.45 wt% catalyst.

Example 17

[0092] Example 5 was repeated, except the fluoropolymer resin pellets of Example 16 were used in place of the resin pellets from Example 4. The resulting film was tested for H₂:O₂ crossover.

Example 18

[0093] Example 3 was repeated, using the pre-hydrolyzed film of Example 17.

Example 19

[0094] Example 13 was repeated, except 250 g of Platinum Black TA HSTDTP with 9 kg of polymer (chemically stabilized PTFE / CF₂=CF-O-CF₂CF(CF₃)-O-CF₂CF₂SO₂F copolymers having an EW of 920 g/mol, available from The Chemours Company, Wilmington, DE) was used, yielding pellets containing 2.77 wt% platinum.

Example 20

[0095] Example 5 was repeated, except the fluoropolymer resin pellets of Example 19 were used in place of the resin pellets from Example 4.

Example 21

[0096] Example 3 was repeated, using the pre-hydrolyzed film of Example 19.

Example 22

[0097] Compositions were prepared by dry mixing 60 grams of sulfonyl fluoride fluoropolymer resin pellets (non-chemically stabilized PTFE / CF₂=CF-O-CF₂CF(CF₃)-O-CF₂CF₂SO₂F copolymers having an EW of 800 g/mol, available from The Chemours Company, Wilmington, DE) and 0.6 grams of Platinum Black TA HSTDTP and feeding the mixture into a Rheometer Services Inc. System 10 batch mixer outfitted with a 60 cc volume mixing bowl containing roller blades. These blends were mixed at 75 rpm at temperatures well above the melting points and/or T_g of the polymer of interest for 10 minutes in order to disperse all the components. In this case, the temperature was 180 °C. The mixtures were then removed from the mixer and subsequently cut into pellets having 1% platinum.

Example 23

[0098] Two separate 1 gallon polyethylene containers were charged with 1.5 kg each of sulfonyl fluoride fluoropolymer resin pellets (chemically stabilized PTFE / $\text{CF}_2=\text{CF}-\text{O}-\text{CF}_2\text{CF}(\text{CF}_3)-\text{O}-\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$ copolymers having an EW of 800 g/mol, available from The Chemours Company, Wilmington, DE). Platinum Black TA HSTDP (54 g) was added to each container. This mixture was roll tumbled for 10 minutes at room temperature to coat the fluoropolymer resin pellets with the platinum. The platinum coated sulfonyl fluoride containing fluoropolymer resin pellets were then fed using a loss-in-weight feeder to a 27 mm diameter twin screw extruder at a polymer feed rate of 6.08 kg/hour and with a screw speed of 100 RPM. The twin screw extruder contained knead block screw elements to help with distributive mixing of the platinum within the fluoropolymer melt. The temperature profile was from 160 °C in the feed throat and increased to 190 °C at the discharge end. Pellets were strand cut to create black pellets containing 3.6 wt% platinum.

Comparative Example A

[0099] A comparative example was prepared with two dispersions of fluoroionomer (hydrolyzed, chemically stabilized PTFE / $\text{CF}_2=\text{CF}-\text{O}-\text{CF}_2\text{CF}(\text{CF}_3)-\text{O}-\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$ copolymers, EW 800 g/mol, available from The Chemours Company, Wilmington, DE), one with HSAPB and the other with no platinum. A 50 µm total membrane, with a 12 µm platinum layer was prepared. The doctor blade was set at a gap to yield a dry film thickness of 12 µm, and the platinized dispersion was solution cast onto a substrate. The cast film and substrate was dried in a relative humidity oven for 30 minutes at 10% RH. The film had a second layer solution cast via doctor blade with non-platinized dispersion at a dry film thickness of 38 µm. The sample was dried in a relative humidity chamber at 10% RH for 30 minutes, then introduced to an oven set at 175 °C for 3 minutes to cure the membrane, yielding a membrane having a Pt content of 20 µg/cm² Pt, based on the weight of the membrane. The platinum-containing solid layer had 1% by weight platinum.

Comparative Example B

[0100] Example 17 was repeated, using only a single layer of non-platinized resin pellets but forming a membrane of the same total thickness.

Table 2. H₂:O₂ Crossover Performance (%) at 0 hours

Current Density (A/cm ²)	Example			
	9	15	17	B
0.1	0.13	0.08	0.44	5.29
0.25	0.09	0.05	0.25	2.61
0.5	0.06	0.03	0.16	1.60
1	0.06	0.03	0.10	1.14
1.5	0.06	0.04	0.08	1.15
2	0.06	0.06	0.06	1.09
3	0.09	0.10	0.09	1.39
4	0.11	0.13	0.24	1.15

[0101] As can be seen in Table 2, the samples show low crossover values compared to a sample containing no platinum content, indicating good initial performance.

[0102] FIGs. 1-7 illustrate membranes having two distinct layers, one having GRC precious metal catalyst and one without additives. It can be seen from FIGs. 1-7 that the current process provides distinct GRC layers having precious metal catalyst uniformly distributed and dispersed throughout the material. This allows coextrusion with a different material layer to form membrane materials having precious metal catalyst with uniform distribution in a desired location while also minimizing the amount of precious metal catalyst needed for the entire membrane. Membranes can be configured to minimize hydrogen and oxygen crossover for multiple end-use applications by purposefully placing the precious metal catalyst in a desired location. By contrast, FIG. 7 shows a membrane formed by a casting process having two layers, where the precious metal catalyst is not uniformly distributed throughout the bottom cast GRC layer. Instead, the precious metal catalyst is agglomerated and concentrated at one side of the GRC cast layer such that it is in contact with the non-GRC layer. Thus, one is not able to customize and configure the layering of precious metal catalyst within the membrane to the effect that it could be done using the present inventive process.

CLAIMS

What is claimed is:

1. A composition comprising about 90% to about 99.99% by weight of one or more non-crosslinked fluorinated sulfonyl fluoride polymers and about 0.01% to about 10% by weight of one or more precious metal catalyst, based on the total weight of the composition, where the one or more precious metal catalyst is uniformly distributed throughout the one or more non-crosslinked fluorinated sulfonyl fluoride polymer.
2. The composition of claim 1, where no solvent or liquid carrier is present.
3. The composition of claim 1, where the one or more precious metal catalyst is unsupported.
4. The composition of claim 1 or 3, where the one or more precious metal catalyst is on a support particle.
5. The composition of claim 4, where the support particle is a carbon, inorganic oxide particle, or mixtures thereof.
6. The composition of claims 1-5, where the one or more precious metal catalyst is selected from platinum, ruthenium, osmium, rhodium, iridium, palladium, or mixtures thereof.
7. The composition of claims 1-6, where the one or more precious metal catalyst is uniformly dispersed throughout the one or more non-crosslinked fluorinated sulfonyl fluoride polymer.
8. The composition of claims 4-5, where the D50 particle size is at most about 5 μm .
9. The composition of claims 1-8, comprising about 92% to about 99.9% by weight of one or more non-crosslinked fluorinated sulfonyl fluoride polymers and about 0.1% to about 8% by weight of one or more precious metal catalyst, based on the total weight of the composition.
10. The composition of claims 1-9, comprising about 95% to about 99.7% by weight of one or more non-crosslinked fluorinated sulfonyl fluoride polymers and about

- 0.3% to about 5% by weight of one or more precious metal catalyst, based on the total weight of the composition.
11. A method of making a solid composition comprising:
 - a. melting at least one non-crosslinked fluorinated sulfonyl fluoride polymer;
 - b. uniformly distributing at least one precious metal catalyst in the at least one molten non-crosslinked fluorinated sulfonyl fluoride polymer in an amount to form a composition comprising about 90% to about 99.99% by weight of one or more non-crosslinked fluorinated sulfonyl fluoride polymers and about 0.01% to about 10% by weight of one or more precious metal catalysts, based on the total weight of the composition;
 - c. cooling the mixture of step b to form a solid composition.
 12. The method of claim 11, where the one or more precious metal catalyst is unsupported.
 13. The method of claim 11, where the one or more precious metal catalyst is on a support particle.
 14. The composition of claim 13, where the support particle is a carbon, inorganic oxide particle, or mixtures thereof.
 15. The method of claims 11-14, where the one or more precious metal catalyst is selected from platinum, ruthenium, osmium, rhodium, iridium, or palladium, or mixtures thereof.
 16. The method of claims 11-15, where the one or more precious metal catalyst is uniformly dispersed throughout the one or more non-crosslinked fluorinated sulfonyl fluoride polymer during step b.
 17. The method of claims 11-16, where the D50 particle size is at most about 5 μm .
 18. The method of claims 11-17, further comprising step b1 of extruding the composition of step b before step c.
 19. A method of making a cation exchange membrane comprising:

- d. melting at least one non-crosslinked fluorinated sulfonyl fluoride polymer;
 - e. uniformly distributing at least one precious metal catalyst with the at least one molten non-crosslinked fluorinated sulfonyl fluoride polymer in an amount to form a composition comprising about 90% to about 99.99% by weight of one or more non-crosslinked fluorinated sulfonyl fluoride polymers and about 0.01% to about 10% by weight of one or more precious metal catalysts, based on the total weight of the composition;
 - f. forming a layer of material from the composition of step e, where the precious metal catalyst is uniformly distributed throughout the layer; and
 - g. converting the non-crosslinked fluorinated sulfonyl fluoride polymer from the layer of step f to a non-crosslinked fluorinated sulfonic acid polymer or non-crosslinked fluorinated sulfonate polymer.
- 20. The method of claim 19, where the one or more precious metal catalyst is unsupported.
 - 21. The method of claim 19, where the one or more precious metal catalyst is on a support particle.
 - 22. The method of claims 19-21, where the one or more precious metal is selected from platinum, ruthenium, osmium, rhodium, iridium, palladium, or mixtures thereof.
 - 23. The method of claims 19-22, where the one or more precious metal catalyst is uniformly dispersed throughout the one or more non-crosslinked fluorinated sulfonyl fluoride polymer during step e.
 - 24. The method of claims 19-23, where the D50 particle size is at most about 5 μm .
 - 25. The method of claims 19-24, where step f occurs by extrusion.
 - 26. The method of claims 19-25, where at least one additional layer is present in the cation exchange membrane.

27. The method of claim 26, where the at least one additional layer comprises an ion exchange resin.
28. The method of claim 27, where the ion exchange resin is a fluorinated sulfonic acid polymer or non-crosslinked sulfonate polymer.
29. The method of claims 26-28, where the at least one additional layer comprises one or more precious metal catalysts.
30. The method of claims 26-28, where the at least one additional layer does not contain precious metal catalyst.
31. The method of claims 26-30, where the at least one additional layer is formed by coextruding the at least one additional layer with the layer of step f to form a single film.
32. The method of claims 26-30, where a third layer is present, and the third layer comprises an ion exchange resin.
33. The method of claim 32, where a fourth layer is present, and the fourth layer comprises an ion exchange resin.
34. The method of claims 32-33, where the third or fourth layers are attached by pressing the layers together at elevated temperature.
35. The method of claims 19-34, further comprising a step e1 of shaping and cooling the composition of step e before step f.
36. The method of claims 19-35, where the composition of step e is applied to a reinforcement material during the layer formation step f or after layer formation step f.
37. The method of claims 19-35, where the cation exchange membrane is unreinforced.
38. A cation exchange membrane made by the method of any of claims 19-37.
39. A cation exchange membrane comprising at least one cation exchange layer, where the at least one cation exchange layer comprises about 90% to about 99.99% by weight of one or more non-crosslinked fluorinated sulfonic acid polymers or non-crosslinked fluorinated sulfonate polymers and about 0.01% to

about 10% by weight of one or more precious metal catalysts, based on the total weight of the composition, where the one or more precious metal catalyst is uniformly distributed throughout the at least one cation exchange layer.

40. The cation exchange membrane of claim 39, where the one or more precious metal catalyst is unsupported.
41. The cation exchange membrane of claim 39, where the one or more precious metal catalyst is on a support particle.
42. The cation exchange membrane of claims 39-41, where the one or more precious metal is selected from platinum, ruthenium, osmium, rhodium, iridium, palladium, or mixtures thereof.
43. The cation exchange membrane of claims 39-42, where the D50 particle size is at most about 5 μm .
44. The cation exchange membrane of claims 39-43, further comprising at least one additional layer in the cation exchange membrane.
45. The cation exchange membrane of claim 44, where the at least one additional layer comprises an ion exchange resin.
46. The cation exchange membrane of claim 45, where the ion exchange resin is a fluorinated sulfonic acid polymer or fluorinated sulfonate polymer.
47. The cation exchange membrane of claims 44-46, where the at least one additional layer comprises one or more precious metal catalysts.
48. The cation exchange membrane of claims 44-46, where the at least one additional layer does not contain precious metal catalyst.
49. The cation exchange membrane of claims 44-48, further comprising a third layer, where the third layer comprises an ion exchange resin.
50. The cation exchange membrane of claim 49, further comprising a fourth layer, where the fourth layer comprises an ion exchange resin.
51. The cation exchange membrane of claims 49-50, where at least one of the third of fourth layers comprises a precious metal catalyst.

52. The cation exchange membrane of claims 49-50, where at least one of the third or fourth layers does not comprise a precious metal catalyst.
53. The cation exchange membrane of claims 39-52, further comprising a reinforcement material in the cation exchange membrane.
54. The cation exchange membrane of claims 39-52, where the cation exchange membrane is unreinforced.
55. A cation exchange membrane precursor comprising at least one cation exchange precursor layer,
where the at least one cation exchange precursor layer comprises about 90% to about 99.99% by weight of one or more non-crosslinked fluorinated sulfonyl fluoride polymers and about 0.01% to about 10% by weight of one or more precious metal catalysts, based on the total weight of the composition, where the one or more precious metal catalyst is uniformly distributed throughout the at least one proton exchange precursor layer.
56. The cation exchange membrane precursor of claim 55, where the one or more precious metal catalyst is unsupported.
57. The cation exchange membrane precursor of claim 55, where the one or more precious metal catalyst is on a support particle.
58. The cation exchange membrane precursor of claims 55-57, where the one or more precious metal is selected from platinum, ruthenium, osmium, rhodium, iridium, palladium, or mixtures thereof.
59. The cation exchange membrane precursor of claims 55-58, where the D50 particle size is at most about 5 μm .
60. The cation exchange membrane precursor of claims 55-59, further comprising at least one additional layer in the cation exchange membrane precursor.
61. The cation exchange membrane precursor of claim 60, where the at least one additional layer comprises an ion exchange resin precursor.
62. The cation exchange membrane of claim 61, where the ion exchange resin precursor is a fluorinated sulfonyl fluoride polymer.

63. The cation exchange membrane precursor of claims 60-62, where the at least one additional layer comprises one or more precious metal catalysts.
64. The cation exchange membrane precursor of claims 60-62, where the at least one additional layer does not contain precious metal catalyst.
65. The cation exchange membrane of claims 60-64, further comprising a third layer, where the third layer comprises an ion exchange resin precursor.
66. The cation exchange membrane of claim 65, further comprising a fourth layer, where the fourth layer comprises an ion exchange resin precursor.
67. The cation exchange membrane of claims 65-66, where at least one of the third or fourth layers comprises a precious metal catalyst.
68. The cation exchange membrane of claim 65-66, where at least one of the third or fourth layers does not comprise a precious metal catalyst.
69. The cation exchange membrane of claims 55-68, further comprising a reinforcement material.
70. The cation exchange membrane of claims 55-68, where the cation exchange membrane is unreinforced.

FIG. 1

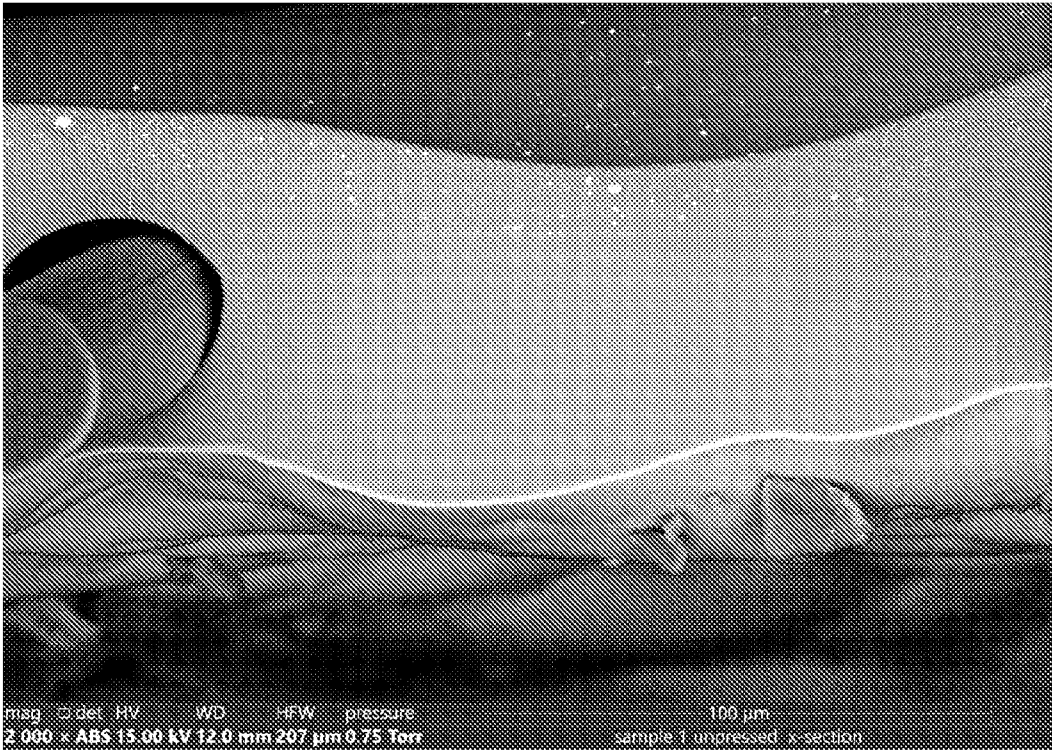


FIG. 2

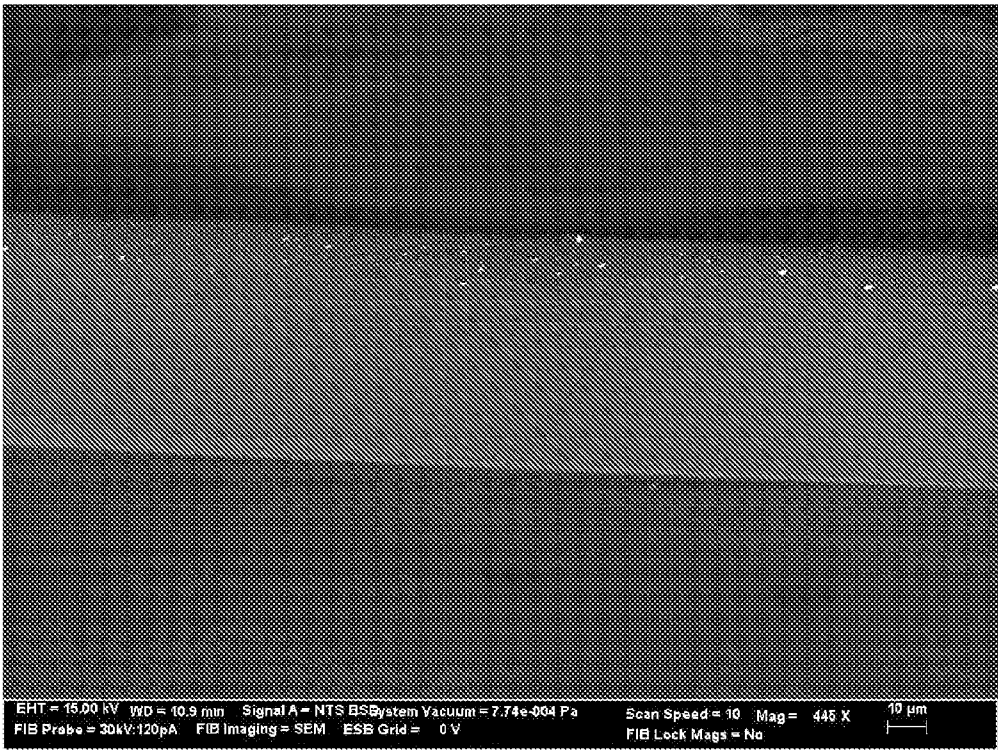


FIG. 3

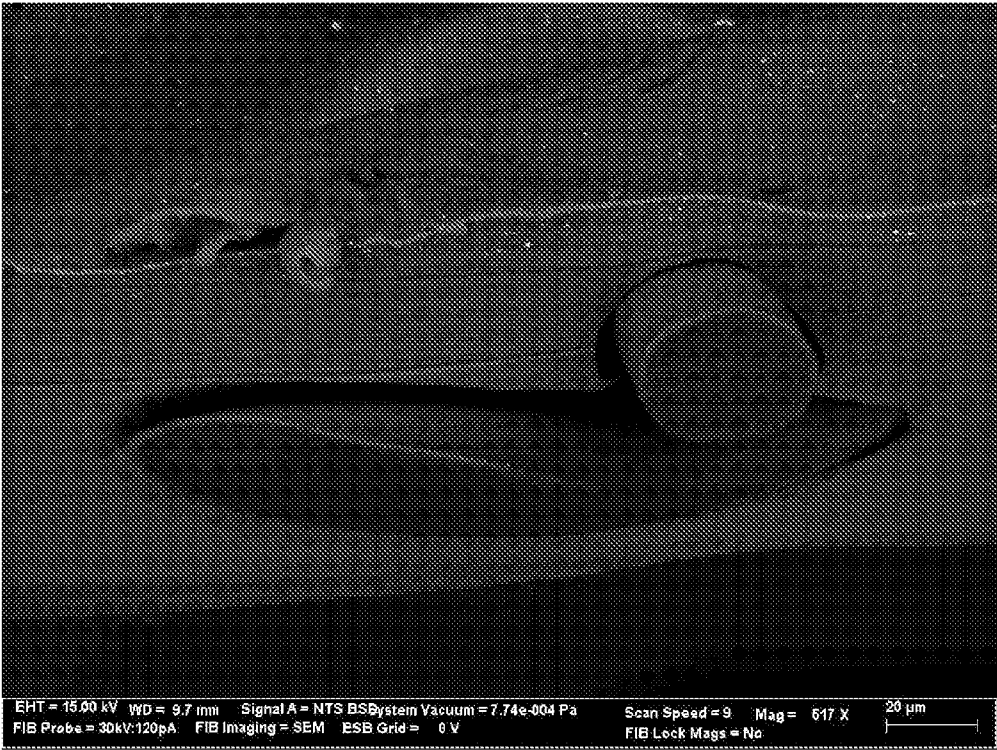


FIG. 4

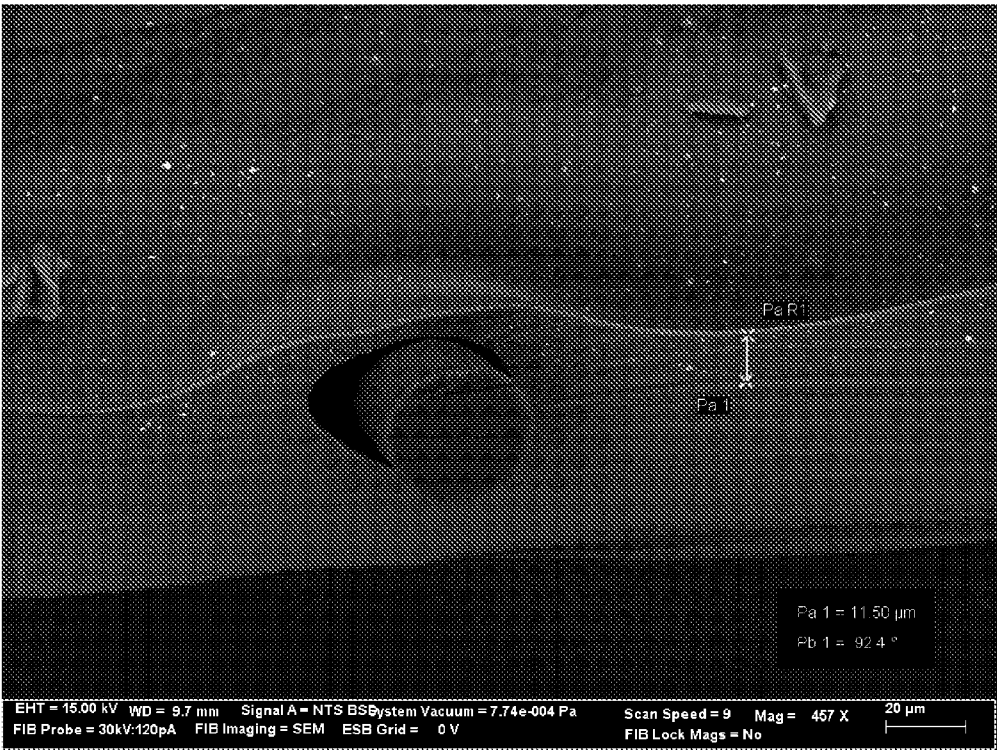


FIG. 5

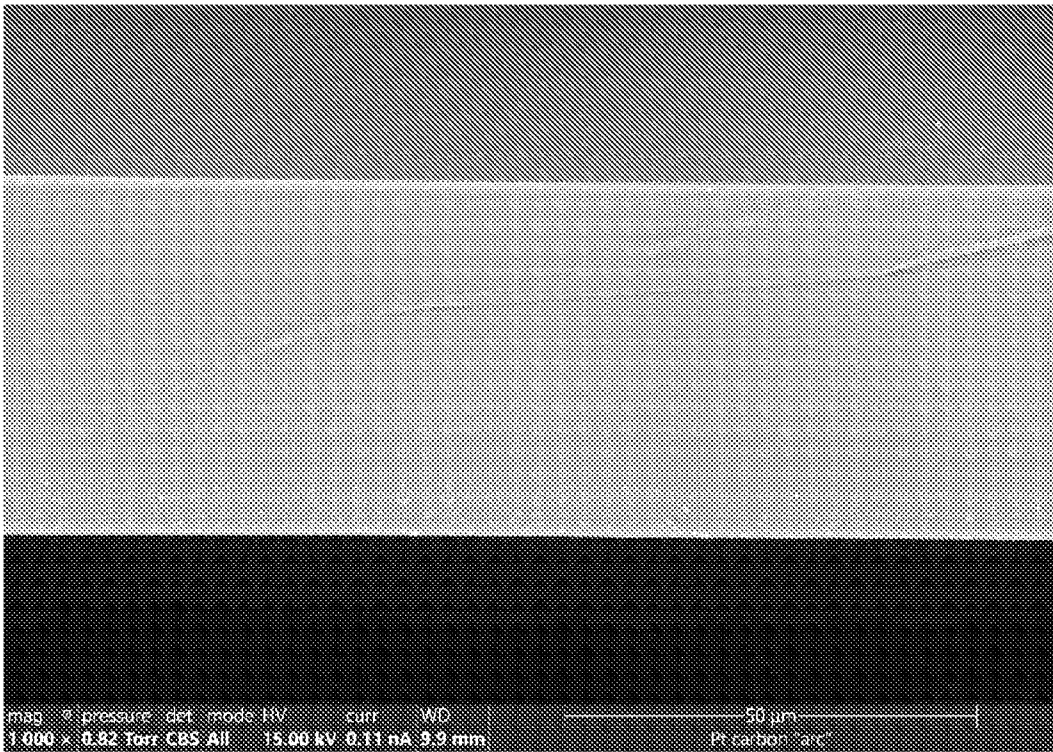


FIG. 6

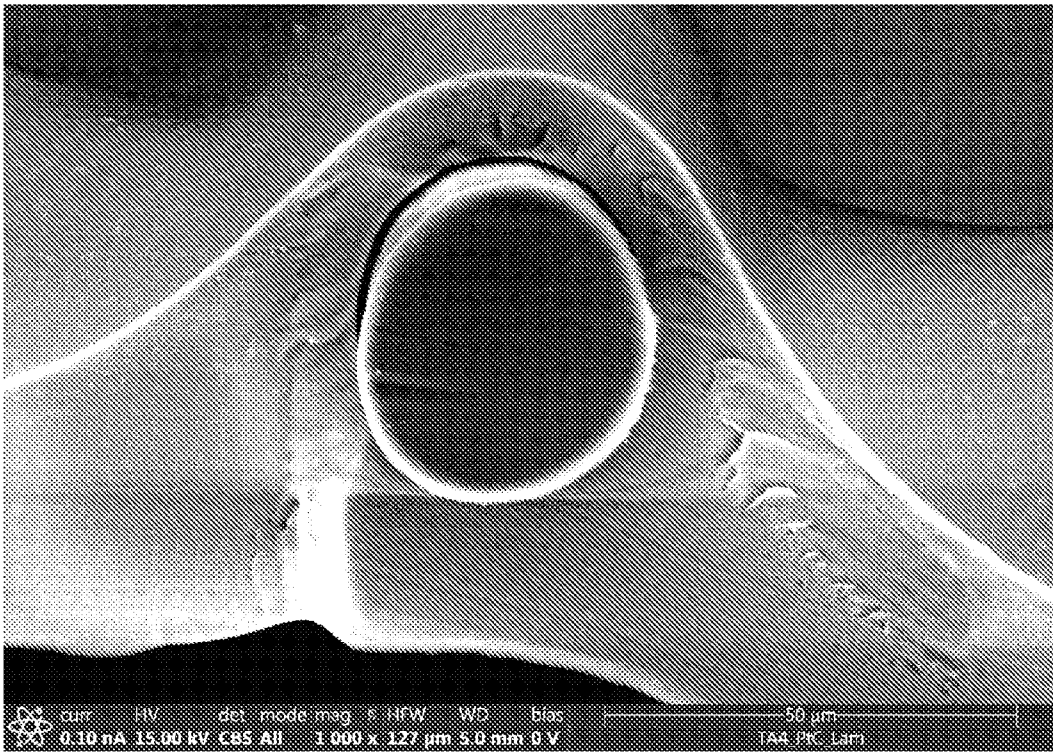
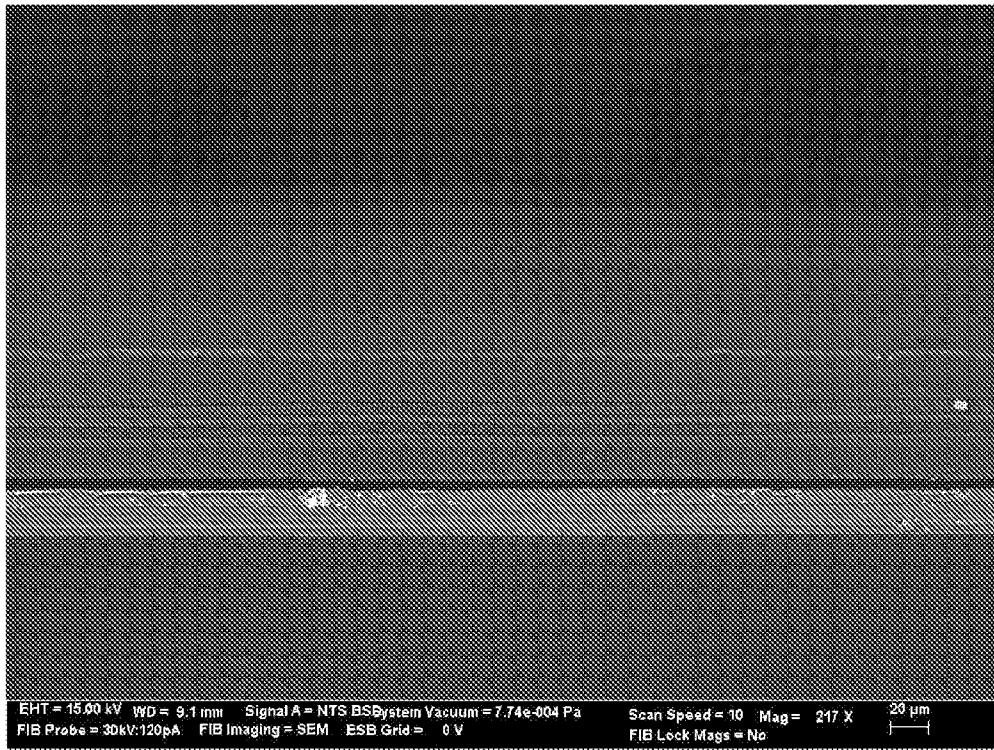


FIG. 7



INTERNATIONAL SEARCH REPORT

International application No

PCT/US2024/021511

A. CLASSIFICATION OF SUBJECT MATTER

INV. C25B1/04 C25B9/23 C25B13/02 C25B13/05 C25B13/08
H01M8/1039 H01M8/1051

ADD.

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)

C25B 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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GARBE STEFFEN ET AL: "Comparison of Pt-Doped Membranes for Gas Crossover Suppression in Polymer Electrolyte Water Electrolysis", JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol. 168, no. 10, 1 October 2021 (2021-10-01), page 104502, XP093110728, ISSN: 0013-4651, DOI: 10.1149/1945-7111/ac2925	38-54
Y	the whole document	1-37, 55-70
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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

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"O" document referring 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

"&" document member of the same patent family

Date of the actual completion of the international search

3 July 2024

Date of mailing of the international search report

17/07/2024

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2024/021511

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HAGIHARA H ET AL: "Preparation of highly dispersed SiO ₂ and Pt particles in Nafion [®] (R)112 for self-humidifying electrolyte membranes in fuel cells", ELECTROCHIMICA ACTA, ELSEVIER, AMSTERDAM, NL, vol. 51, no. 19, 20 May 2006 (2006-05-20), pages 3979-3985, XP025168842, ISSN: 0013-4686, DOI: 10.1016/J.ELECTACTA.2005.11.012	38-54
Y	the whole document	1-37, 55-70

X	ZHANG ZHEYU ET AL: "Platinum and Cerium-Zirconium Oxide Co-Doped Membrane for Mitigated H ₂ Crossover and Ionomer Degradation in PEWE", JOURNAL OF THE ELECTROCHEMICAL SOCIETY, ELECTROCHEMICAL SOCIETY, vol. 169, no. 10, 10 October 2022 (2022-10-10), XP009548704, ISSN: 0013-4651, DOI: 10.1149/1945-7111/AC94A3	38-54
Y	the whole document	1-37, 55-70

X	MOKRINI ASMAE ET AL: "Investigation of Advanced Hybrid PEM Based on Sulfonfyl Fluoride PFSA and Grafted Inorganic Nanoparticles", ECS TRANSACTIONS, vol. 33, no. 1, 1 October 2010 (2010-10-01), pages 823-838, XP093180660, US	38-54
Y	ISSN: 1938-5862, DOI: 10.1149/1.3484576 the whole document	1-37, 55-70

A	KWAK S-H ET AL: "The effect of platinum loading in the self-humidifying polymer electrolyte membrane on water uptake", JOURNAL OF POWER SOURCES, ELSEVIER, AMSTERDAM, NL, vol. 118, no. 1-2, 25 May 2003 (2003-05-25), pages 200-204, XP004425682, ISSN: 0378-7753, DOI: 10.1016/S0378-7753(03)00094-6	1-64
	the whole document	
