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(71) Applicants (for all designated States except US): **ARKE-MA INC.** [US/US]; 2000 Market Street, Philadelphia, Pennsylvania 19103 (US). **VIRGINIA TECH INTELLECTUAL PROPERTIES, INC.** [US/US]; 2200 Kraft Drive, Suite 1050, Blacksburg, Virginia 24060 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **MOUNTZ, David, A.** [US/US]; 288 Fox Run, Exton, Pennsylvania 19341 (US). **GOLDBACH, James, T.** [US/US]; 267 Orchard Road, Paoli, Pennsylvania 19301 (US). **MCGRATH, James, E.** [US/US]; 902 Elliot Drive, Blacksburg, Virginia 24060 (US). **MICHEL, Sophie M. V.** [FR/FR]; 27 Avenue Jeanne d'Arc, Apt. 103, 38100 Grenoble (FR).

(74) Agents: **ROLAND, Thomas, F.** et al.; Arkema Inc., 2000 Market Street, Philadelphia, Pennsylvania 19103 (US).

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(57) Abstract: The invention relates to blends of polyvinylidene fluoride (PVDF) polymers and copolymers with sulfonated poly(ether sulfones) (SPES) useful in forming of membranes. The SPES polyelectrolyte is immobilized within the PVDF matrix. These membranes are useful under hydrated conditions, and may find use as membranes in fuel cells, water purification, humidification and battery separators. The invention also relates to a method for producing stable, homogeneous blends of PVDF and SPES, and useful membranes of those blends.



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BLEND OF POLYVINYLIDENE FLUORIDE COPOLYMERS WITH SULFONATED POLY(ETHER SULFONES)

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- 5 Department of Energy (NO. DE-FG36-07GO17008) and the U.S. Government may have certain rights in this invention.

Filed of the Invention

- 10 The invention relates to blends of polyvinylidene fluoride (PVDF) polymers and copolymers with sulfonated poly(ether sulfones) (SPES) useful in forming of membranes. The SPES polyelectrolyte is contained within the PVDF matrix. These membranes are useful under hydrated conditions, and may find use as membranes in fuel cells, water purification, humidification and battery separators. The invention also relates to a method for producing stable, homogeneous blends of PVDF and
- 15 SPES, and useful membranes of those blends.

Background of the Invention

- Membranes, such as fuel cell membranes, battery membranes and water purification membranes may be exposed to very harsh acidic or basic media at
- 20 temperatures that can reach 200°C, in an oxidizing and/or reducing environment due to the presence of metal ions and sometimes presence of solvents. This environment requires that the membrane be chemically and electrochemically resistant, as well as thermally stable.

- Professor McGrath at Virginia Tech has investigated the synthesis and use of
- 25 sulfonated poly(arylene ether sulfone) (SPES) copolymers with pendent sulfonic acid groups as proton exchange membranes. (US 7,361,729; US 2005/0261442; US 2006/0036064; US 2006/0258836; US 2007/0292730). These references are incorporated herein by reference. These membranes have been shown to be applicable as fuel cell membranes provided that the molar amount of protogenic (typically
- 30 sulfonate) groups present remains below a critical value. SPES materials bearing larger fractions of protogenic groups suffer from poor mechanical properties and exorbitant levels of swelling when they are exposed to liquid water or elevated relative humidity conditions.

- Polyelectrolytes may be blended with fluoropolymers, such as poly(vinylidene
- 35 fluoride) (PVDF) homopolymer and copolymers, in order to improve physical,

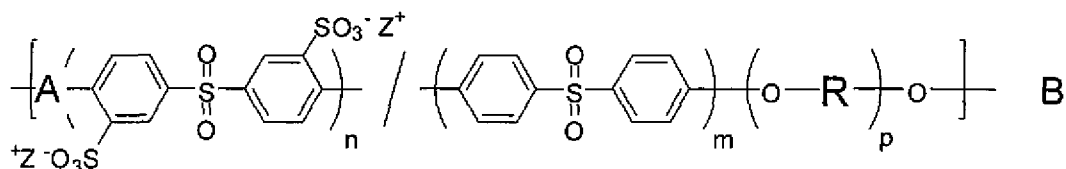
chemical, and electrochemical properties to form membranes. Polyelectrolytes bearing a wide range of functionalities can be successfully incorporated into PVDF (such as Kynar[®] resin) blends by carefully controlling the processing parameters utilized; providing that the polyelectrolytes bear a significant fraction of protogenic
5 (acidic) units such as sulfonates, phosphonates, or carboxylates. The blends in the form of membranes could be used in fuel cells, water purification, humidification, and battery separators. See US 6,872,781; US 6,780,935; and US 7,449,111, all incorporated herein by reference.

The applicants have now found that blending SPES materials with PVDF can
10 provide membranes having increased mechanical strength and reduced swelling of articles or films produced from these blends. Blending also allows for the use of SPES having higher levels of protogenic groups. In addition, the highly aromatic chemical nature of the SPES polyelectrolytes may provide for increased chemical and/or thermal stability.

15 One problem with membranes formed from blends including polyelectrolytes having higher levels of protogenic groups, is that they can be soluble in water. Since many of the uses for these membranes is in highly humidified or water-immersed conditions, it is important that the polyelectrolytes remain in the PVDF blend over time, to retain the desired ion conductivity and mechanical properties. This problem
20 has been solved by immobilizing the polyelectrolyte in the PVDF matrix through the use of covalent cross-linking of the polyelectrolyte, introduction of preferential interaction of the polyelectrolyte with the matrix, physical interpenetration of polyelectrolyte chains with the matrix polymer chains, or any combination thereof. Immobilization of the polyelectrolyte in the matrix (co)polymer is a key factor in
25 producing viable membranes to be used under hydrated conditions.

Summary of the Invention

The invention relates to a polyelectrolyte composition having a copolymer of a sulfonated bisaryl monomer, a non-sulfonated bisaryl monomer, and a diol monomer,
30 where the counterions present on the sulfonated bisaryl monomer are quaternary ammonium or phosphonium having the formula:



where:

Z = a positively charged quaternary ammonium or phosphonium counterion of C4 to C32, or a proton, or a mixture of aforementioned counterion and proton wherein the proportion of counterion to proton is from 50 to 100 mol%.

R = alkyl, aryl, bisaryl, (per)fluoroalkyl, (per)fluoroaryl, or (per)fluorobisaryl of C1 to C16

A = an end group

B = an end group

n,m,p = mol fractions of each monomer where $n+m+p=1$.

The invention also relates to a polymer blend of this polyelectrolyte with a matrix polymer. The matrix polymer is preferably a fluorinated polymer, with poly(vinylidene fluoride) preferred.

Detailed Description of the Invention

The invention relates to blends of polyvinylidene fluoride (PVDF) polymers and copolymers with sulfonated poly(ether sulfones) (SPES), and to membranes formed from the blend.

SPES

The SPES materials of the invention are generally synthesized by condensation copolymerization of a sulfonated bisaryl sulfone monomer with an aromatic diol co-monomer in a ratio of 1:1. A third co-monomer can be added (typically, a non-sulfonated bisaryl sulfone) such that the molar amount of sulfone monomers equals that of the diol monomer. A generalized reaction and structure for a typical SPES copolymer is shown in Figure 1. The ratio of sulfonated sulfone monomer to non-sulfonated sulfone co-monomer can be varied to adjust the final content of sulfonate functionality present in the material. The content of sulfonate functionality thus affects the material's ability to absorb water and conduct protons. In one embodiment, a ratio of about 2:3 of sulfonated sulfone to non-sulfonated sulfone

is used to provide a maximum proton conductivity with minimized dimensional change (swelling).

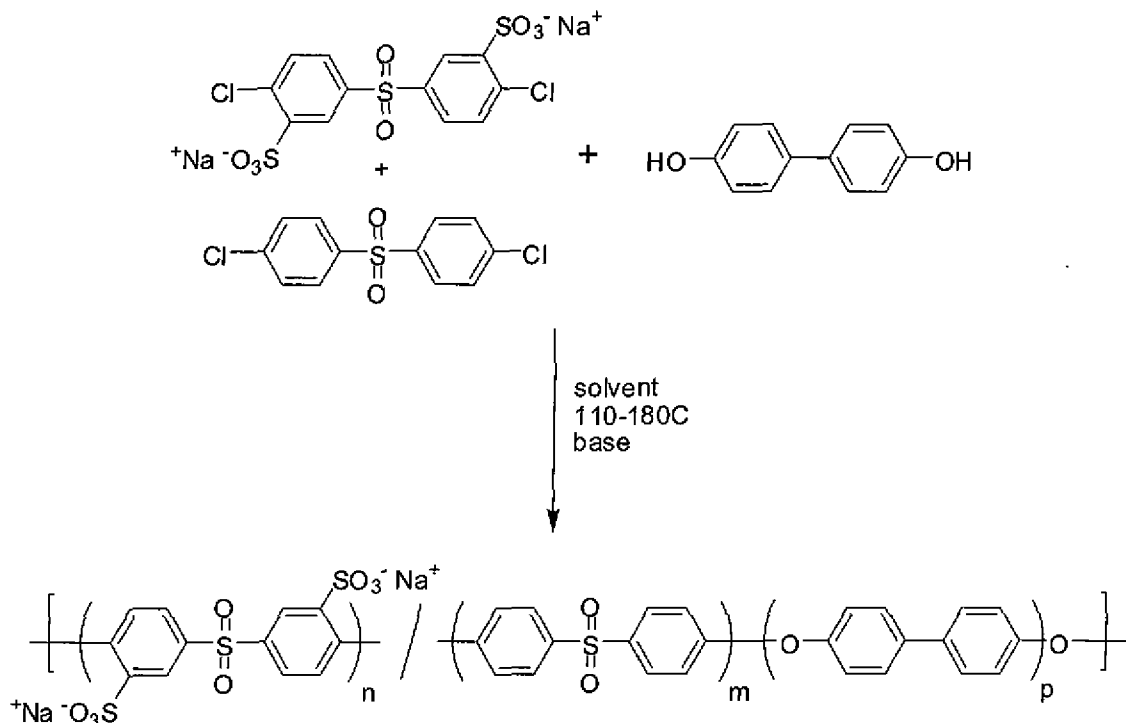


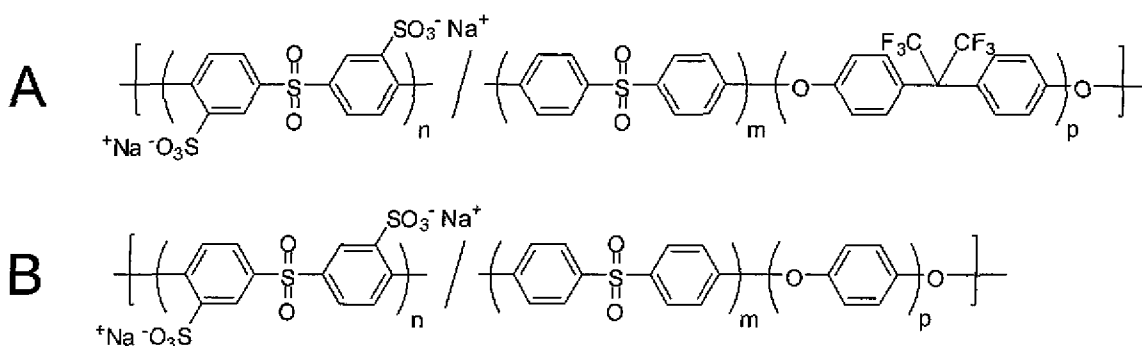
Figure 1. **Synthesis of SPES copolymers. ($n+m=p$) (For SPES-100, $n=1$, $m=0$, $p=1$; for SPES-40, $n=2$, $m=3$, $p=5$)**

A somewhat atypical nomenclature is used in the literature to identify the sulfonation level in SPES materials. A SPES material containing a ratio of 1:1 of sulfonated sulfone monomer to diol monomer is termed SPES-100, meaning that 100% of the sulfone monomer is sulfonated (while pertaining to only 50 mol.-% of the overall monomer units). When a non-sulfonated sulfone monomer is incorporated, the SPES-XXX number is decreased according to the molar amount of sulfonated monomer present in the material. For example, SPES-40 contains a ratio of sulfone monomers of 40 mol.-% sulfonated to 60 mol.-% non-sulfonated (while pertaining to overall molar ratios of 20 mol.-% sulfonated sulfone, 30 mol.-% non-sulfonated sulfone, and 50 mol.-% diol).

In addition to the above reaction scheme for the synthesis of SPES copolymers, the nature of the diol monomer can be varied. The synthetic strategy and requirements for the stoichiometry of sulfone and diol monomer remain the same, however, the chemical nature of the diol can vary, and alternate nomenclature is used:

6F-XX: refers to the copolymer of sulfone monomer with hexafluoro bisphenol A as diol comonomer. XX refers to the mol percentage of sulfonated sulfone to non-sulfonated sulfone monomer present (Figure 2A).

- 5 **HQS-XX**: refers to the copolymer of sulfone monomer with hydroquinone as diol comonomer. XX refers to the mol percentage of sulfonated sulfone to non-sulfonated sulfone monomer present (Figure 2B).



- 10 **Figure 2.** Structures of copolymers containing alternate diols as comonomer. **A:** 6F-40, where hexafluoro Bisphenol A is used as diol comonomer and $n=2$, $m=3$, $p=5$. **B:** HQS-40, where hydroquinone is used as diol comonomer and $n=2$, $m=3$, $p=5$.

- SPES compositions presently used in the art for fuel cell applications are
- 15 SPES-35 and SPES-40, as SPES materials bearing larger fractions of protogenic groups suffer from poor mechanical properties and high swelling when they are exposed to liquid water or elevated relative humidity conditions.

PVDF Blending

- 20 The polymer blend of the present invention is an intimate blend of SPES with a fluoropolymer. Preferably, the attachment between the SPES and the fluoropolymer is a physical attachment though attachments other than physical attachments are within the bounds of the present invention including chemical attachments. The amount of fluoropolymer can be from about 5 to about 95 weight % and the amount
- 25 of the SPES can be from about 95 to about 5 weight %. Preferably, the fluoropolymer is present in an amount of from about 20% to about 70 weight % and the amount of SPES is from about 30 to about 80 weight %.

With respect to the fluoropolymer, this fluoropolymer can be a homopolymer or other type of polymer, and can be a mixture of fluoropolymers or a

mixture of fluoropolymer with a non-fluoropolymer. Preferably, a thermoplastic fluoropolymer is used. Preferably, this fluoropolymer or mixture of fluoropolymers can be any fluoropolymer(s) that can form a polymer blend with the other components, including other polymers present. Preferably, the fluoropolymer is a poly(vinylidene fluoride) polymer such as a poly(vinylidene fluoride) homopolymer. Other examples of fluoropolymers include, but are not limited to, a poly(alkylene) containing at least one fluorine atom, such as polytetrafluoroethylene, poly(vinyl fluoride), poly(vinylidene fluoride-*co*-hexafluoropropylene), poly(vinylidene fluoride-*co*-fluorinated vinyl ether), poly(tetrafluoroethylene-*co*-fluorinated vinyl ether), poly(fluorinated alkylene-*co*-vinyl ether) or combinations thereof. More preferably, the fluoropolymer is a polymeric composition containing from about 30% to about 100 weight % of vinylidene fluoride and from 0% to about 70 weight % of at least one poly(alkylene) containing at least one fluorine atom, such as, hexafluoropropylene, tetrafluoroethylene, trifluoroethylene (VF3), chlorotrifluoroethylene, and/or vinyl fluoride. Preferably, the weight average molecular weight (MW) of the fluoropolymer, which can include homopolymers, copolymers, terpolymers, oligomers, and other types of polymers, is from about 80,000 MW to about 1,000,000 MW and, more preferably from about 100,000 MW to about 500,000 MW. The fluoropolymers can be prepared using the techniques described in U.S. Patent Nos. 3,051,677; 3,178,399; 3,475,396; 3,857,827; and 5,093,427, all incorporated herein in their entirety by reference.

The blending process of the matrix polymer and SPES preferably involves the conversion of the protogenic/acidic groups into a tetraalkylammonium (TAA)-neutralized form. This can be achieved through various processes known in the art. Preferably the ammonium salt has a molecular weight of at least 186. Examples of suitable ammonium salts include: tetramethylammonium, tetraethylammonium, tetrapropylammonium, tetrabutylammonium, tetrapentylammonium, tetrahexylammonium, and asymmetric-type moieties such as trioctyltrimethylammonium or benzyltrimethylammonium.

A solution of this TAA-neutralized polyelectrolyte is then prepared in an appropriate solvent which may appropriately dissolve the matrix (co)polymer of choice. As stated above, the amount of matrix polymer can be from 5 to 95 weight % and the amount of polyelectrolyte can be from 95 to 5 weight % in the blend solution. Preferably, the matrix polymer is present in an amount of from 30% to 80 weight %

and the polyelectrolyte is present at from 20 to 70 weight % in the blend solution. This blended solution is then cast into a thin film or further processed to yield a useful article such as an ion-exchange membrane.

As described previously, a fuel cell membrane must exist and operate in highly humidified or liquid water environments. Given this fact, it is of utmost importance that the hydrophilic portion(s) of the membrane material be immobilized such that they are not lost to the environment by dissolution and/or leaching. When films of SPES materials (alone) are used as membranes, the amount of sulfonated sulfone monomer must be optimized to provide for sufficient proton conductivity while minimizing dimensional change (x-y swelling) due to water uptake. This trade-off imposes a practical maximum amount of sulfonated sulfone monomer that can be used in a given copolymer.

Cross-linking of the SPES material can provide a means of linking all of the polymer molecules together, immobilizing them, and reducing the amount of dimensional change in the overall material. Cross-linking, as used here, means that the polymer bears functional groups that are capable of reacting with each other or with another reagent to produce a network of covalently bonded polymer. SPES materials bear few cross-linkable functional groups, however, adding additional diol monomer as a final step in the polymerization reaction can control the nature of the chain end groups. This effectively ensures that each end group bears one phenol functionality that can be used for further reaction (introduction of cross-linkable functionality). Incorporation of such a cross-linking functionality potentially will allow for the use of higher sulfonated sulfone monomer content SPES materials, while maintaining low material dimensional change and low or no loss of material by leaching.

In one embodiment, a SPES copolymer is reacted with excess diol monomer upon completion of the polymerization. This phenol-capped material is further reacted with a tetraepoxide compound to incorporate an alcohol as well as multi-epoxide functionality at each end group. Thermal treatment of this material affects further ring opening of the epoxides, presumably by reaction with the existing alcohol groups. When inter-chain reactions occur, polymer cross-linking results.

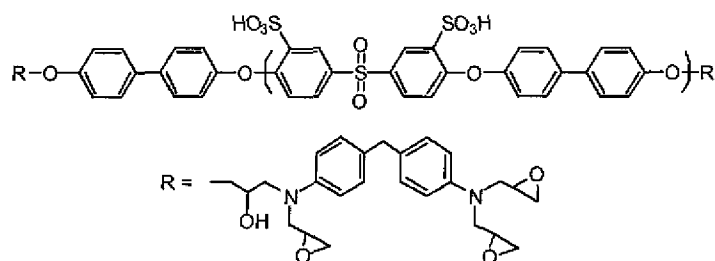


Figure 3. Depiction of a SPES-100 material bearing epoxide cross-linkable end groups.

A key feature of the present invention is the ability to cross-link the polyelectrolyte portions of the polymer blend. This is typically achieved by any number of methods known to those skilled in the art. The method chosen will depend on the chemical nature and structure of the polyelectrolyte as well as the functional groups available to participate in the cross-linking reaction. In general, it is desired that the cross-linking result in functional groups that fulfill the same requirement as were set for the rest of the copolyelectrolyte. These include, but are not limited to: hydrolytic, thermal, and free-radical-attack stability. In addition, it is of utmost importance that the cross-linking reaction not occurs prematurely, i.e. prior to film casting and formation. If this were to occur, film casting may not be possible and a non-homogeneous, non-uniform product may result. It is most preferred that the cross-linking reaction take place by either the introduction (and activation) of an external agent, termed the 'cross-linking agent' or 'cross-linker', or by the application of an external stimulus such as heat, UV radiation, or electron beam. It is also possible that the cross-linking be afforded by a combination of these methods such as would occur for the addition of a UV-active sensitizer to the blend with subsequent UV irradiation of the film. The point at which the cross-linking occurs is of utmost importance. The reaction must be controllable such that a uniform film may be cast, with subsequent activation of the cross-linking. The application of the cross-linking may occur prior to or post drying of the wet film.

Membrane Formation

Casting of the blended solution can be carried out by many different procedures familiar to those skilled in the art, such as extrusion, molding, solvent casting, and latex casting. The formed film or membrane may be used as a single layer, or may be part of a multi-layer film or membrane. A preferred method is solution casting with heating. The thickness of the formed, wet film before drying is dependent on the end-use of the material, and can vary from 1.0 μm to 2.0mm. Preferably, the formed film has a thickness of 10.0 μm to 500.0 μm and most preferably from 20.0 μm to 500.0

μm. This 'wet' film is then dried in a air-circulating oven at elevated temperature.

The time and temperature for drying the film can vary widely. The temperature used is from 20 °C to 250 °C, preferably from 100 °C to 220 °C, and most preferably from 120 °C to 200 °C. The drying time for the wet film can also vary widely. The oven
5 residence time should be commercially applicable and scalable in that it can be from 1.0 s to 24 h, preferably from 1.0 min. to 2.0 h, and most preferably from 1.0 min. to 45.0 min.

The thickness of the final, dried film depends on the original thickness of the wet film before drying. This thickness will vary depending on the application
10 intended for the final article. The thickness can be from 1.0 μm to 2.0 mm, preferably from 5.0 μm to 500.0 μm, most preferably from 10.0 μm to 300.0 μm. The dried film is removed from the substrate by typical methods familiar to those skilled in the art.

The domain size of the polyelectrolyte in a cast film should be preferably less than 1.0 μm, and more preferably between 1 nm to 500 nm. The domain sizes
15 discussed herein are with respect to maximum domain sizes and/or average domain sizes. In a preferred embodiment, the domain sizes recited are the maximum domain sizes, but can be the average domain sizes.

The proton conductivity of the polymer blend of the invention is >10 mS/cm, preferably >50 mS/cm, and most preferably >100 mS/cm. Additionally, the polymer
20 blend has a high degree of mechanical strength, a low swelling when hydrated, hydrolytic (chemical) stability, and a low level of sulfur loss (if sulfonated) in hot water, hot acid, oxidizing and/or reducing environments.

An article, such as a membrane, produced from the polymer blend of the invention can be used as-is or further treated by an acidic washing step to remove the
25 tetraalkyl groups, concurrently reprotonating the ionizable groups present on the starting (co)polymer component.

Due to the various advantages described above, the applications of the present invention can include, but are not limited to, films, membranes, fuel cells, coatings, ion exchange resins, oil recovery, biological membranes, batteries, and the like. The
30 resultant articles can be utilized as perm-selective membranes for fuel cell or battery applications. In addition, the resultant articles may be applied to electrodes for the construction of a membrane-electrode-assembly, may be imbibed with various

liquids, or may be introduced onto or into a reinforcing matte or porous web to increase mechanical integrity.

Examples

5

All polymer solutions were cast into membrane using a Mathis LTE Labdryer. 2 mil thick aluminum foil with approximate dimensions of 15x12 inches was used as the substrate for casting. Approximately 15g of polymer solution was spread on the foil and drawn down to a wet film thickness of about 300 micron using a doctor blade.

10 The resulting wet film was then heated at either 177°C for 7 minutes or 200°C for 3.5 minutes. The oven blower was set a 2000 RPM. The dry membranes were then removed from the oven and cooled to room temperature. The thickness of the dried membranes was between 20-50 microns.

15 The membrane conductivity was measured using the following procedure. Membrane samples were cut from a 1x6 cm rectangular die and boiled in 18 MΩ deionized water for one hour. After cooling, the membranes were mounted in four point probe conductivity cells constructed of acrylic and 0.5 mm platinum wire. Impedance data was collected at 70°C in 18 MΩ deionized water using a Gamry PC4/300 Potentiostat
20 connected to a 6 channel multiplexor. Conductivity was calculated using dimensions of the sample, inner electrode distance of the conductivity cell, and the sample impedance at 1000 Hz (conductivity = inner electrode distance/(impedance*sample thickness*sample width).

25 **Example 1: SPES-40 / Kynar® PVDF resin**

The SPES-40 used in this example had 40 mol% disulfonation (determined by proton NMR) and an intrinsic viscosity of 0.9 dl/g (measured in a solution containing 0.05M LiBr in 1-methyl-2-pyrrolidinone). Approximately 10g of potassium
30 counterion-form SPES-40 was dissolved in 1-methyl-2-pyrrolidinone (NMP) to make a 10 wt% solution. The solution was cast into a membrane using the procedure and equipment described above. Potassium counterion-form membrane was then immersed in 2200g of 1M aqueous hydrochloric acid. The acid bath was heated from ambient to 60-65°C over the span of approximately 75 min. The bath was then held
35 in this temperature range for approximately 45 minutes. Subsequently, the membrane

was washed in 18 MΩ deionized water and immersed in 2200g of 1M sulfuric acid. The acid bath was heated from ambient to 60-65°C over the span of approximately 75 min. The bath was then held in this temperature range for approximately 45 minutes. The membranes were removed from the sulfuric acid bath and washed with 18 MΩ
5 deionized water to remove residual acid. The acid-form membranes were then dried at room temperature under vacuum.

2.00g of the dried SPES-40 membrane was dissolved in dimethyl acetamide to produce a 10 wt% solution. 1.207g of aqueous 55 wt% tetrabutyl ammonium hydroxide was added to the polyelectrolyte solution. The solution was placed on a
10 rotary evaporator to remove all of the water introduced to by adding the base solution. 8.88 g of a 15 wt % solution of Kynar® PVDF 2801 in dimethyl acetamide was added to the neutralized polyelectrolyte solution. The Kynar PVDF/polyelectrolyte solution was then mixed overnight with magnetic stirring at room temperature.

The solution was cast into a membrane as described above. The membrane
15 was released from the aluminum foil substrate by immersing it in warm deionized water. The membrane was then protonated in 2200g of 1M aqueous hydrochloric acid. The acid bath was heated from ambient to 60-65°C over the span of approximately 75 min. The bath was then held in this temperature range for approximately 45 minutes. Subsequently, the membrane was washed in 18 MΩ
20 deionized water and immersed in 2200g of 1M sulfuric acid. The acid bath was heated from ambient to 60-65°C over the span of approximately 75 min. The bath was then held in this temperature range for approximately 45 minutes. The membranes were removed from the sulfuric acid bath and washed with 18 MΩ deionized water to remove residual acid. The acid-form membrane was then dried at
25 room temperature. The resulting membrane had a proton conductivity of 15mS/cm.

Example 2: SPES-60 / Kynar PVDF resin

The SPES-60 used in this example had 57 mol% disulfonation (determined by
30 proton NMR) and a number average molecular weight of 27 kg/mol and a PDI of 1.5 (determined by GPC using a mobile phase of NMP with 0.5% LiBr at 60°C using universal calibration curve constructed from polystyrene standards). 9.87g of potassium counterion-form SPES-60 was dissolved in 40.12g of NMP (n-methyl pyrrolidinone). Films were cast using the equipment described above at 80°C,

700RPM for 60 minutes. These films were released from the substrate by immersion in 18 MΩ deionized water. These films were then converted to the acid form by immersing them in 1L of 1M hydrochloric acid at 80°C for four hours. The films were rinsed three times with 1L of 18 MΩ deionized water until the pH reached 6. These
5 films were dried overnight in vacuum room at 35°C.

1.04g of proton-form SPES-60 was dissolved in NMP. 1.03g of 55 wt% tetrabutylammonium hydroxide was added to get 99% neutralization of the acid groups. The water was removed by rotary evaporating and the solution blended with 1.74g of Kynar® PVDF 2801 (15 wt % dissolved in NMP). The solution was stirred
10 for three hours with a mechanical stirring. Membranes were cast from the solution as described previously.

The membranes were released from the substrate by immersion in 18 MΩ deionized water. These films were then protonated in 1 liter of 1M hydrochloric acid for two hours at 65°C with stirring. The membranes were washed twice with
15 deionized water and immersed in 1 liter of 1M sulfuric acid for two hours at 65°C under stirring. They were rinsed three times with 1 liter deionized water until the pH reached 6. The acid form membranes were dried at room temperature and their conductivity was 54 mS/cm.

20 **Example 3: SPES-100 / Kynar PVDF resin**

The SPES-100 used in this example had a weight average molecular weight of 27 kg/mol and a PDI of 1.5 (determined by GPC using a mobile phase of water with 0.10 M NaNO₃ at 35°C using universal calibration curve constructed from sulfonated
25 polystyrene standards). 40.0g of potassium counterion-form SPES-100 was dissolved in 360.0g of deionized water. To a 6in. diameter glass column equipped with a bottom plug of glass wool and stopcock was added 1.5L of Dowex Marathon C ion-exchange resin. This resin was twice washed with 2.0L of deionized water, and allowed to soak in deionized water for 18h. The resin was then washed with an additional 2.0L of
30 deionized water, at which time the pH of the eluent was 6.0 as measured with pH paper (EM Science, pH range 0-14). The 400.0g of SPES-100 solution was then poured into the ion-exchange column taking care to not disturb the resin. The SPES-100 solution was then drained through the column and the pH of the eluent was monitored by periodically measuring pH using pH paper as before. Fractions of pH <

2.0 were collected. Additional deionized water was added to the column to elute residual material. A total of 3.5L of acidic solution was collected. This solution was then added to a 5L three-necked round-bottom flask equipped with heating mantle, temperature feedback controller (J-Kem 210), nitrogen inlet, and mechanical stirrer.

- 5 The solution was heated to 60 °C with mechanical stirring and slight flow of dry nitrogen. In this fashion, 2L of water was removed by evaporation. Acid content was determined by triplicate titration with 0.1047M potassium hydroxide standard solution to phenolphthalein endpoint. The average acid content was determined to be 0.116 mmol H⁺/g solution. Polymer concentration was determined in duplicate by
- 10 drying ~10g samples of acidified solution under vacuum (10⁻³ torr). An average solution concentration was determined to be 1.28 wt.-% polymer in water.

39.70g of aqueous 55 wt% tetrabutylammonium hydroxide solution was added to 928.11g of acid-form SPES-100 solution. The solution was stirred and had a final pH of 4.67. 135.4g of NMP was added to the neutralized polyelectrolyte solution and

15 the resulting solution was placed on a rotary evaporator to remove the water. The final solution of neutralized polyelectrolyte in NMP had a solids level of about 24wt%.

16.263g of the neutralized polyelectrolyte solution was combined with 16.291g of a 15wt% solution of Kynar[®] PVDF 2801 in NMP. The Kynar

20 PVDF/polyelectrolyte solution was then mixed for three hours with magnetic stirring at room temperature. The resulting solution was cast into a membrane as described previously.

The membrane was released from the substrate by immersing it in warm deionized water. It was then exchanged to proton-form as described in Example 1.

- 25 The acid-form membrane was then dried at room temperature. The resulting membrane was transparent and a conductivity of 75mS/cm.

Example 4: 6F-45 / Kynar PVDF resin

- 30 The 6F-45 used in this example had 44 mol% disulfonation (determined by proton NMR) and an intrinsic viscosity of 0.7 dl/g (measured in a solution containing 0.05M LiBr in 1-methyl-2-pyrrolidinone). Potassium counterion-form 6F-45 was dissolved in NMP to make a 20 wt% solution. The solution was cast into a membrane using the procedure and equipment described above. It was then exchanged to the

proton counterion-form as described in Example 1. The proton-form membranes were then dried at room temperature under vacuum.

1.50 g of the dried membrane was dissolved in dimethyl acetamide to produce a 20 wt% solution. 95 mole% of the acid groups (calculated from film mass and the chemical composition determined from NMR) were neutralized with aqueous 55 wt% tetrabutylammonium hydroxide solution. The solution was placed on a rotary evaporator to remove all of the water introduced to by adding the base solution. 7.23g of a 15 wt% solution of Kynar[®] PVDF 2801 in dimethyl acetamide was added to the neutralized polyelectrolyte solution. The Kynar PVDF/polyelectrolyte solution was then mixed overnight with mechanical stirring at room temperature.

The solution was cast into a membrane as described above. The membrane was released from the substrate by immersing it in warm deionized water. It was then exchanged to the proton counterion-form as described in Example 1. This membrane was then dried at room temperature. The resulting membrane had a proton conductivity of 16mS/cm.

Example 5: 6F-60 / Kynar PVDF resin

2.98g of potassium counterion-form 6F-60 materials were dissolved in 12.11g of NMP. The solution was cast at 80C, 700rpm for 60 minutes as described above. The films were released by immersion in 18 MΩ deionized water. The films were exchanged to proton-form as described in Example 2.

0.87g of SPES6F60 films were dissolved in NMP to make a 20 wt% solution. 0.69g of 55 wt% tetrabutylammonium hydroxide were added to neutralize the acid groups. The solution was stirred and the water removed by rotary evaporation. 1.69g of 15wt % solution of Kynar PVDF 2801 was added and the solution was stirred for two hours with magnetic stirring. Membranes were cast as described above and released by immersion in 18 MΩ deionized water. The membranes were exchanged to the proton counterion-form using the method described in Example 2.

Example 6: Crosslinkable epoxide-functionalized SPES-100 / Kynar[®] PVDF resin

The SPES-100 used in this example contains functionalized, thermally-activated end-groups as depicted in Figure 3 and had a number average molecular weight of 20 kg/mol and a PDI of 1.9 (determined by aqueous GPC, 35°C vs.

sulfonated polystyrene standards). This polymer was synthesized in the potassium salt form. The potassium ions were replaced with tetrabutylammonium ions using an ion exchange column. The procedure for the ion exchange is the same as Example 3, except that the Dowex Marathon C ion-exchange resin had been pre-reacted with an excess of tetrabutylammonium hydroxide solution and washed with deionized water until the pH of the wash water was measured as neutral beforehand.

40.63g of NMP was added to 439.94g of aqueous solution of tetrabutylammonium form SPES-100 (solution contained 22.26g of tetrabutylammonium form SPES-100). The water was then removed by rotary evaporation. 10.45g of this NMP solution was blended with 24.78g of 15 wt% solution of Kynar PVDF 2801 and stirred for two hours with a mechanical stirrer. The solution was cast into a membrane as described above at 200°C for 10 minutes. The membrane was then exchanged to the proton counterion-form using the method described in Example 2. The resulting membrane had a proton conductivity of 26mS/cm.

Example 7: Cross-linkable amine-functionalized SPES-100/ Kynar PVDF resin

The SPES-100 used in this example contains amine endgroups that may be cross-linked by reacting the polymer with a curing agent containing epoxide groups. The procedure for functionalizing the SPES-100 with amine groups is described by Lee *et al.* (J. Polym. Sci. Part A Polym. Chem., **2007**, *45*, 4879-4890). The SPES-100 had a number average molecular weight of 5.0 kg/mol (as determined by proton NMR) and an amine functionality of approximately 2.0 (the chain end-groups). The polymer was synthesized with the sulfonate groups in the potassium form. The ions on the sulfonate groups were exchanged to tetrabutylammonium (TBA) using the same method described for Example 6. Proton NMR was used to determine that approximately 100% of the ions were exchanged to TBA.

34.91g of NMP was added to 129.96g of aqueous solution of TBA-form SPES-100 (solution contained 8.01g of tetrabutylammonium form SPES-100). The water was then removed by rotary evaporation. 5.69g of this NMP solution was then blended with 1.91g of 21 wt% solution of Kynar® PVDF 2801 and 0.0254g of 4,4'-methylenebis (N,N-diglycidylaniline). 0.256g of a solution containing 0.1 wt% 2-ethylimidazole in NMP was also added to the formulation. The solution was stirred

for approximately two hours with a mechanical stirrer and then cast into a membrane as described above at 210°C for 20 minutes.

The membranes were released from the casting substrate by immersion in 18 MΩ deionized water. They were then protonated in 3 liters of 1M hydrochloric acid with stirring. During the protonation, the acid was heated from ambient to 80°C over approximately 75 minutes and then held at that temperature for 30 minutes. The membranes were washed with deionized water and immersed in 3 liters of 1M sulfuric acid using the same heating profile as the hydrochloric acid. The membranes were then rinsed with three, one-liter charges of deionized water until the pH reached 6. The resulting membrane was dried at room temperature and had a proton conductivity of 145mS/cm.

Example 8: Cross-linkable amine-functionalized SPES-100/ Kynar PVDF resin

The amine-functionalized SPES-100 used in this example was the same as Example 7. 34.91g of NMP was added to 129.96g of aqueous solution of tetrabutylammonium (TBA) form SPES-100 (solution contained 8.01g of tetrabutylammonium form SPES-100). The water was then removed by rotary evaporation. 5.48g of this NMP solution was then blended with 4.14g of 21 wt% solution of Kynar PVDF 2801 and 0.0245g of 4,4'-methylenebis (N,N-diglycidylaniline). 0.246g of a solution containing 0.1 wt% 2-ethylimidazole in NMP was also added to the formulation. The solution was stirred for approximately two hours with a mechanical stirrer and then cast into a membrane as described above at 210°C for 20 minutes.

The membranes were released from the casting substrate by immersion in 18 MΩ deionized water and protonated as described in Example 7. The resulting membrane was dried at room temperature after the protonation and had a proton conductivity of 109mS/cm.

Example 9: Cross-linkable ethynyl-functionalized SPES-100/ Kynar® PVDF resin

The SPES-100 used in this example contains ethynyl end-groups that thermally cross-link. Ethynyl-terminated SPES-100 was synthesized by reacting phenoxide-terminated SPES-100 with 4-ethyl-4'-fluorobenzophenone in a solution of

dimethylacetamide and cyclohexane with potassium carbonate at 140°C for 3 hours. The 4-ethyl-4'-fluorobenzophenone was synthesized using a procedure published by Belfort *et al.* (J. Polym. Sci. Part A Polym. Chem., 1990, 28, 2451-2464).

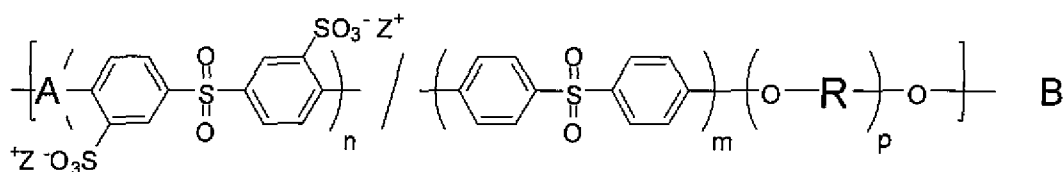
The functionalized SPES-100 had a number average molecular weight of 4 kg/mol (as determined by proton NMR) and an ethynyl functionality of approximately 2 (the chain end-groups). The polymer was synthesized with the sulfonate groups in the potassium form. The ions on the sulfonate groups were exchanged to tetrabutylammonium using the same method described for Example 6. Proton NMR was used to determine that 80 mol.-% of the ions were exchanged to TBA.

4.4g of NMP was added to 59.58g of aqueous solution of tetrabutylammonium form SPES-100 (solution contained 1.65g of tetrabutylammonium form SPES-100). The water was then removed by rotary evaporation. The entire solution was then blended with 6.96g of 21 wt% solution of Kynar PVDF 2801. The solution was stirred for approximately two hours with a mechanical stirrer and then cast into a membrane as described above at 250°C for 30 minutes.

The membranes were released from the casting substrate by immersion in 18 MΩ deionized water and protonated as described in Example 7. The resulting membrane was dried at room temperature after the protonation and had a proton conductivity of 127mS/cm.

What is claimed is:

1. A polyelectrolyte composition comprising a copolymer of a sulfonated bisaryl monomer, a non-sulfonated bisaryl monomer, and a diol monomer, wherein the counterions present on the sulfonated bisaryl monomer are quaternary ammonium or phosphonium having the formula:



where:

- Z = a positively charged quaternary ammonium or phosphonium counterion of C4 to C32, or a proton, or a mixture of aforementioned counterion and proton wherein the proportion of counterion to proton is from 50 to 100 mol%.
 R = alkyl, aryl, bisaryl, (per)fluoroalkyl, (per)fluoroaryl, or (per)fluorobisaryl of C1 to C16

A = an end group

- 15 B = an end group

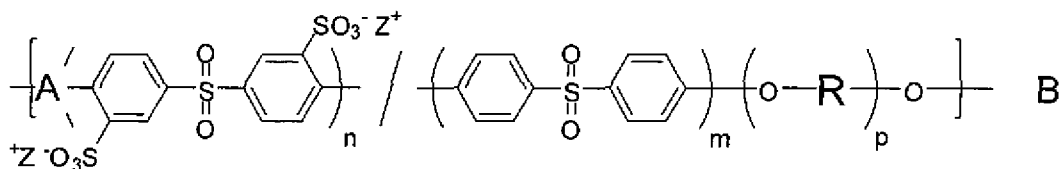
n,m,p = mol fractions of each monomer where n+m = p.

2. The polyelectrolyte composition of a Claim 1 wherein the amount of sulfonated bisaryl monomer relative to non-sulfonated bisaryl monomer ranges from 20 to 100 mol%, preferably from 50 to 500 mol%.

3. The polyelectrolyte composition of Claim 1 wherein one or more of the end-groups are cross-linkable.

- 25 4. A polymer blend comprising:

a) 1 to 99 weight percent of a polyelectrolyte composition comprising a one or more copolymers of a sulfonated bisaryl monomer, a non-sulfonated bisaryl monomer, and a diol monomer, wherein the counterions present on the sulfonated bisaryl monomer are quaternary ammonium or phosphonium, having the formula:



where:

Z = a positively charged quaternary ammonium or phosphonium counterion of C4 to C32, or a proton, or a mixture of aforementioned counterion and proton wherein the proportion of counterion to proton is from 50 to 100 mol%.

5 R = alkyl, aryl, bisaryl, (per)fluoroalkyl, (per)fluoroaryl, or (per)fluorobisaryl of C1 to C16

n,m,p = mol fractions of each monomer where $n+m = p$.

A = an end group capable of crosslinking the polyelectrolyte.

B = an end group capable of crosslinking the polyelectrolyte.

10 b) 1 to 99 weight percent of a matrix polymer,
wherein said polyelectrolyte and matrix polymer are different, and wherein a) and b) polymers form a blend, and wherein the polyelectrolyte is partially or fully cross-linked.

15 5. The polymer blend of claim 4, comprising 15 to 98 weight percent of polyelectrolyte (a) and from 2 to 85 weight percent of the matrix polymer (b).

6. The polymer blend of claim 4, comprising 15 to 50 weight percent of polyelectrolyte (a) wherein the proportion of n to (n+m) is from 20 to 50%, and from
20 50 to 85 weight percent of matrix polymer (b).

7. The polymer blend of claim 5, comprising 20 to 50 weight percent of polyelectrolyte (a) and from 50 to 80 weight percent of the matrix polymer (b).

25 8. The polymer blend of claim 5, comprising 20 to 50 weight percent of polyelectrolyte (a) wherein the proportion of n to (n+m) is from 45 to 80%, and from 50 to 80 weight percent of matrix polymer (b).

9. The polymer blend of claim 5, comprising 20 to 50 weight percent of
30 polyelectrolyte (a) wherein the proportion of n to (n+m) is from 80 to 100%, and from 50 to 80 weight percent of matrix polymer (b).

10. The polymer blend of Claim 4 wherein the matrix copolymer is fluorinated.

35 11. The polymer blend of Claim 4 wherein the matrix copolymer is poly(vinylidene fluoride) homopolymer or copolymer.

12. A film or membrane article comprising the polymer blend of claim 4.
13. The article of claim 12, wherein said article is a fuel cell, humidification
5 device, water purification device, or battery.
14. A membrane-electrode assembly comprising the film or membrane of Claim
12.
- 10 15. A fuel cell comprising the membrane-electrode assembly of Claim 14.
16. The film or membrane article of claim 12, wherein the counter ion (Z) of said
polymer blend comprises protons.
17. The film or membrane article of claim 16, wherein 50 to 100 % of the (Z)
15 counter ions are protons.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2010/031001

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01M 8/10 (2010.01)

USPC - 526/326; 429/12

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)

IPC(8) - H01M 8/10; C08F 16/06 (2010.01)

USPC - 526/326; 429/12, 30

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)

MicroPatent, Freepatentsonline, Google

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2006/0166048 A1 (SAKAGUCHI et al) 27 July 2006 (27.07.2006) entire document	1-17
Y	US 2007/0122676 A1 (SONG) 31 May 2007 (31.05.2007) entire document	1-17
A	US 2005/0031925 A1 (OFER et al) 10 February 2005 (10.02.2005) entire document	1-17
A	US 2008/0242819 A1 (GOLDBACH) 02 October 2008 (02.10.2008) entire document	1-17

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

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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

26 May 2010

Date of mailing of the international search report

16 JUN 2010

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Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Blaine R. Copenheaver

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774