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(71) Applicant(s): L&T TECHNOLOGY SERVICES LIMITED

(72) Inventor(s): Mondal, Ujjal
Patil, Tushar Vilas
Patel, Aumkumar
Pednekar, Akash Avinash
Jampangire, Vishnu

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(54) Title: EFFICIENT AND NOVEL HIGH TEMPERATURE POLYMER ELECTROLYTE MEMBRANE COMPOSITION FOR FUEL CELL APPLICATIONS

(57) Abstract: The present invention relates to a high temperature proton exchange membrane composition to enhance the stability and efficiency of fuel cells & electrolyzers at high temperature applications. The present invention also relates to the method of synthesizing membrane composition. The combinations of AB-PBI, task specific dicationic liquids, MCF, and phosphoric acid will improve the ionic conductivity at higher temperatures, provide higher resistance to impurities, provides good chemical stability, good thermal stability, good mechanical stability. The compositions are easily disposable, environment friendly and do not require any humidification for proton transfer.

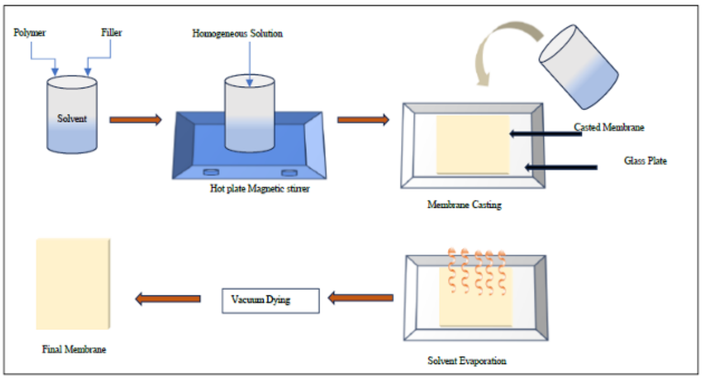

Figure 1

FORM 2

THE PATENTS ACT 1970
(39 OF 1970)
&
The Patent Rules, 2003

Complete Specification

(See Section 10 and Rule 13)

1. TITLE OF THE INVENTION

EFFICIENT AND NOVEL HIGH TEMPERATURE POLYMER ELECTROLYTE MEMBRANE COMPOSITION FOR FUEL CELL APPLICATIONS

2. APPLICANT(S)

(a) NAME : **L&T TECHNOLOGY SERVICES LIMITED**
(b) NATIONALITY : **INDIAN**

(c) ADDRESS : **DLF IT SEZ Park, 2nd Floor – Block 3**
1/124, Mount Poonamallee Road,
Ramapuram, Chennai – 600 089,
INDIA.

3. PREAMBLE TO THE DESCRIPTION

COMPLETE

The following specification particularly describes the invention and the manner in which it is to be performed

DESCRIPTION

FIELD OF THE INVENTION

[0001] The present invention relates to a membrane composition using ionic liquids and inorganic additives to enhance the stability and efficiency of fuel cells & electrolyzers at high temperatures. The present invention also relates to a method of preparing membrane composition to achieve desired membrane properties at high temperature.

BACKGROUND OF THE INVENTION

[0002] Global leaders set a goal of Net-Zero emissions by 2050 to curb the global warming to 1.5 ℃ from preindustrial level. Carbon dioxide is one of the major heat-trapping pollutants, called greenhouse gas. The presence of CO_2 in the atmosphere absorbs and insulates heat, creating an invisible vail that keeps sun's energy from escaping into outer space, resulting increasing temperature of earth's surface. To tackle the issue of global warming lower CO_2 emitting process should be adopted by various industries.

[0003] Hydrogen, being the most abundant element in the universe, can become the perfect fuel since by burning hydrogen water vapors are produced instead of carbon dioxide. Use of hydrogen would drastically reduce the emissions responsible for the greenhouse effect and global warming.

[0004] Fuel cells & electrolyzers are considered as one of the important sources for achieving the targets of green economy now a days. Hydrogen produced by the electrolyzer in sustainable way, i.e. without emitting carbon dioxide into the atmosphere.

[0005] Polymer electrolyte membrane/proton exchange membrane (PEM) is a crucial component of electrolyzer and fuel cells. PEM fuel cell technology is widely used in various sectors. However, there are several limitations of these technology such as operating at various temperature since the performance of the membrane is optimal in a certain range of temperature (typically 60-80°C).

[0006] Currently Naflon is used as a membrane in PEM fuel cell. It is a perfluorosulfonic acid (PFSA) membrane based on a PFSA/polytetrafluoroethylene (PTFE) copolymer. As they come under "forever chemicals" category they should be avoided. These membranes operate at temperature range of 80 ºC and cannot be used above 100 ºC as it begins to degrade at a faster rate at higher temperature. The LT-PEMFC (Low temperature PEM fuel cell) has a very low tolerance to impurities in fuel, (it requires 99.99999% pure hydrogen) which is expensive to produce. The heat produced from the LT-PEMFC is also at low temperature and thus is difficult to transfer away for use in other processes and due to the nature of the membrane, drying out of the MEA, both of which lead to a loss in performance. Operating the PEM FC at higher temperature range (120-180°C) allows co-generation of heat and power, high tolerance to fuel impurities and simpler system design.

[0007] Therefore, there is a need to develop a novel composition of solid polymer electrolyte which can be operated at high temperatures and maintain mechanical and chemical integrity at high temperatures with improved proton conductivity.

OBJECTIVE OF THE INVENTION

[0008] Main objective of the present invention is to provide a membrane composition to enhance the stability and efficiency of fuel cells & electrolyzers.

[0009] The objective of the present invention is to provide two task specific ionic liquid to enhance the properties of fuel cells & electrolyzers.

[0010] Another objective of the present invention is to provide a method of preparing membrane composition to enhance the stability and efficiency of fuel cells & electrolyzers.

[0011] Yet another objective of the present invention is to provide a composition, method for preparing the composition to improve ionic conductivity at higher temperatures, provide higher resistance to impurities, provides good chemical stability, good thermal stability, good mechanical stability.

[0012] Still another objective of the present invention is to provide a composition which is easily disposable, environment friendly and does not require any humidification for proton transfer.

SUMMARY OF THE INVENTION

[0013] Main aspect of the present invention provides a membrane composition to enhance the stability and efficiency of fuel cells & electrolyzers.

[0014] The aspect of the present invention provides two task specific ionic liquid to enhance the stability and efficiency of fuel cells & electrolyzers.

[0015] Another aspect of the present invention provides a method of preparing membrane composition to enhance the stability and efficiency of fuel cells & electrolyzers.

[0016] Yet another aspect of the present invention provides a composition, method for preparing the composition to improve ionic conductivity at higher temperatures, provide higher resistance to impurities, provides good chemical stability, good thermal stability, good mechanical stability.

[0017] Still another aspect of the present invention provides a composition which is easily disposable, environment friendly and does not require any humidification for proton transfer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] Fig 1: Represents method of preparing membrane composition.

<u>DETAILED DESCRIPTION OF THE INVENTION</u>

[0019] Main embodiment of the present invention provides a membrane composition comprising:

- Aromatic Polybenzimidazole;
- Amine-functionalized Mesocellular Foam (MCF);
- Phosphoric Acid; and
- Ionic Liquids.

[0020] The embodiment of the present invention provides the composition, wherein the aromatic polybenzimidazole is selected from AB-PBI, SPEEK, PFSA, m-PBI.

[0021] Another embodiment of the present invention provides the composition, wherein the amine-functionalized mesocellular foam is selected from SBA-15, MCM-41, MCM-48, CNT, GO.

[0022] Yet another embodiment of the present invention provides the composition, wherein the ionic liquids are engineered from conventional and task specific ionic liquids.

[0023] Yet another embodiment of the present invention provides the composition, wherein the dicationic ionic liquid is selected from 3,3'-(1,2-ethanediyl) bis[1-(4-sulfobutyl)-1H-imidazolium bis(trifluoromethane)sulfonimide) [ESBI]-[TFSI], [BMIM]-[CL], [BMIM]-[BR], [EMIM]-[CL], [BMIM]-[NTF2], [EMIM]-[TFSI].

[0024] Yet another embodiment of the present invention provides the composition, wherein the tricationic ionic liquid is selected from 1,3-di(3-methylimidazolium) propane bis(trifluoromethylsulfonyl) imide [DMIP]-[NTF2], [ESBI]-[TFSI], [BMIM]-[CL], [BMIM]-[BR], [EMIM]-[CL], [BMIM]-[NTF2], [EMIM]-[TFSI].

[0025] Yet another embodiment of the present invention provides the composition, wherein the amount of aromatic polybenzimidazole is in the range of 80 to 98%.

[0026] Yet another embodiment of the present invention provides the composition, wherein the amount of amine-functionalized mesocellular foam is in the range of 0.5 to 5%.

[0027] Yet another embodiment of the present invention provides the composition, wherein the amount of ionic liquids is in the range of 1 to 10%.

[0028] Yet another embodiment of the present invention provides the composition, wherein the amount of phosphoric acid is in the range of 5 to 20%.

[0029] Yet another embodiment of the present invention provides a membrane composition comprising:

- AB-PBI;
- NH2-MCF;
- Phosphoric Acid; and
- [ESBI][TFSI].

[0030] Yet another embodiment of the present invention provides a membrane composition comprising:

- 80-98 % of AB-PBI;
- 0.5-5% of NH2-MCF;
- 5-20% of Phosphoric Acid; and
- 1-10% of [ESBI][TFSI].

[0031] Yet another embodiment of the present invention provides a membrane composition comprising:

- AB-PBI;
- NH2-MCF;
- Phosphoric Acid; and
- [DMIP][NTF2].

[0032] Yet another embodiment of the present invention provides a membrane composition comprising:

- 80-98 % of AB-PBI;
- 0.5-5% of NH2-MCF;
- 5-20% of Phosphoric Acid; and
- 1-10% of [DMIP][NTF2].

[0033] Yet another embodiment of the present invention provides a di cationic ionic liquid 3,3'-(1,2-ethanediyl) bis[1-(4-sulfobutyl)-1H-imidazolium bis(trifluoromethane)sulfonimide) [ESBI]-[TFSI].

[0034] Yet another embodiment of the present invention provides a tri cationic ionic liquid 1,3-di(3-methylimidazolium) propane bis(trifluoromethylsulfonyl) imide [DMIP]-[NTF2].

[0035] Yet another embodiment of the present invention provides a method of preparing membrane composition, wherein the method comprising the following steps:

i. Dissolving the aromatic polybenzimidazole powder in dimethylacetamide (DMAc) or MSA (Methane Sulfonic Acid) solvent, followed by heating to obtain an aromatic polybenzimidazole/DMAc or MSA solution;

ii. Adding the ionic liquids into the aromatic polybenzimidazole/DMAc or MSA solution obtained in step i), followed by stirring the mixture to get the homogeneous solution;

iii. Adding amine-functionalized mesocellular foam into the homogeneous solution obtained in step ii), followed by sonication;

iv. Degassing the solution obtained in step iii) to obtain the casting solution;

v. Casting the solution onto a glass plate to form a film, followed by drying the cast film to get a solid membrane;

vi. Immersing the solid membrane obtained in step v) in a Phosphoric Acid (PA) solution.

[0036] Yet another embodiment of the present invention provides a method, wherein the heating in step i) was carried out in the teflon-lined bomb reactor.

[0037] Yet another embodiment of the present invention provides a method, wherein the heating in step i) was carried out at 50 °C to 150 °C.

[0038] Yet another embodiment of the present invention provides a method, wherein the heating in step i) was carried out for 2 to 4 hours.

[0039] Yet another embodiment of the present invention provides a method, wherein in step ii) the ionic liquid was added in the range of 0 to 10% w/w with respect to the pristine PBI polymer.

[0040] Yet another embodiment of the present invention provides a method, wherein in step ii) stirring was carried out for 1 to 4 hours.

[0041] Yet another embodiment of the present invention provides a method, wherein in step iii) the amount of amine-functionalized mesocellular foam was in the range of 0 to 10% w/w concerning the pristine AB-PBI polymer.

[0042] Yet another embodiment of the present invention provides a method, wherein in step iii) sonication was carried out for 10 to 30 minutes.

[0043] Yet another embodiment of the present invention provides a method, wherein in step iii) sonication was carried out at 30-50 °C.

[0044] Yet another embodiment of the present invention provides a method, wherein in step iv) degassing was carried out for 10 to 30 minutes.

[0045] Yet another embodiment of the present invention provides a method, wherein in step v) the casting the solution onto a glass plate was carried out by a digital casting knife.

[0046] Yet another embodiment of the present invention provides a method, wherein in step v) the casting was uniform casting.

[0047] Yet another embodiment of the present invention provides a method, wherein in step v) the drying was carried out at 100 to 200 °C.

[0048] Yet another embodiment of the present invention provides a method, wherein in step vi) the immersing was carried out at 30 to 40 °C.

[0049] Yet another embodiment of the present invention provides a method, wherein in step vi) the immersing was carried out for 5 to 7 days.

[0050] Yet another embodiment of the present invention provides a method, wherein in step vi) the concentration of PA (Phosphoric Acid) solution was 70 to 85%.

[0051] Yet another embodiment of the present invention provides a membrane composition to enhance the stability and efficiency of fuel cells & electrolyzers.

[0052] Yet another embodiment of the present invention provides two task specific ionic liquid to enhance the stability and efficiency of fuel cells & electrolyzers.

[0053] Yet another embodiment of the present invention provides a composition, method for preparing the composition to improve ionic conductivity at higher temperatures, provide higher resistance to impurities, provides good chemical stability, good thermal stability, good mechanical stability.

[0054] Yet another embodiment of the present invention provides a composition which is easily disposable, environment friendly and does not require any humidification for proton transfer.

[0055] Yet another embodiment of the present invention provides a composition which can be operated at high temperatures and maintain mechanical and chemical integrity at high temperatures with improved proton conductivity.

<u>EXPERIMENTAL SECTION:</u>

[0056] **<u>Materials</u>**: Following Materials were used in the present invention:

- AB-PBI (Aromatic Polybenzimidazole) powder
- DMAc (Dimethylacetamide) or MSA solvent
- Di-cationic ILs (Dicationic Ionic Liquids)
- Amine-functionalized Mesocellular Foam (NH2-MCF)
- Glass plate
- Digital casting knife
- Teflon-lined bomb reactor
- Phosphoric Acid solution
- Nitrogen gas supply

[0057] **<u>Method of Preparing Membrane Composition</u>**:

The method of preparing membrane composition (as also shown in Figure 1) comprising the following steps:

1. <u>Preparation of AB-PBI/DMAc</u> or MSA <u>Solution:</u>

- Placing the AB-PBI powder in the teflon-lined bomb reactor.
- Adding DMAc or MSA solvent to the reactor until it covers the AB-PBI powder.
- Sealing the reactor securely and ensure it is airtight.
- Purging the reactor with nitrogen gas to create an inert atmosphere.

- Heating the reactor to 50-150°C and maintain this temperature for up to 4 hours to dissolve the AB-PBI in DMAc or MSA thoroughly.

2. Incorporating Di-cationic ILs:

- After dissolving AB-PBI, introducing different amounts of Di-cationic ILs (in the range of 0-10% w/w with respect to the pristine PBI polymer) into the AB-PBI/DMAc or MSA solution.
- Vigorously stirring the mixture for up to 4 hours within the teflon-lined bomb reactor to ensure a homogenous blend of the components.

3. Adding Amine-Functionalized MCF:

- Slowly introducing amine-functionalized Mesocellular Foam (NH2-MCF) into the homogeneous solution of AB-PBI and Di-cationic ILs, in amounts ranging from 0-10% w/w concerning the pristine AB-PBI polymer.
- Sonicating the mixture for 30 minutes at 30 to 50°C to enhance the dispersion of NH2-MCF within the solution.
- Performing the degassing for up to 30 minutes to remove any entrapped air within the solution.

4. Casting Solution Preparation:

- The obtained solution from the teflon-lined bomb reactor is now the casting solution. It includes the dissolved AB-PBI, Di-cationic ILs, and NH2-MCF.

5. Film Casting:

- Using a digital casting knife to uniformly cast the solution onto a glass plate. This step ensures the formation of a thin, even film.

6. Drying Under Vacuum:

- Drying the cast films at 100 to 200 °C under vacuum conditions until no significant weight loss is observed in the membranes. This ensures the complete evaporation of the DMAc or MSA solvent and the formation of a solid membrane.

7. Membrane Immersion:

- Immersing the prepared membranes in a PA (Phosphoric Acid) solution with 70 to 85% concentration for 5 to 7 days at 30-40 °C. This step is crucial for conditioning the membrane for high-temperature fuel cell applications.

WE CLAIM:

1. A membrane composition comprising:
    - Aromatic Polybenzimidazole;
    - Amine-functionalized Mesocellular Foam;
    - Ionic Liquids; and
    - Phosphoric Acid

Dated this 12th day of November 2024

--Digitally Signed--
Bhanu Prasad (INPA No: 3253)
Head, IPR Dept.,
L&T Technology Services Limited,
DLF 3rd Block, 2nd Floor,
Manapakkam, Chennai, TN, 600089.

ABSTRACT

EFFICIENT AND NOVEL HIGH TEMPERATURE POLYMER ELECTROLYTE MEMBRANE COMPOSITION FOR FUEL CELL APPLICATIONS

The present invention relates to a high temperature proton exchange membrane composition to enhance the stability and efficiency of fuel cells & electrolyzers at high temperature applications. The present invention also relates to the method of synthesizing membrane composition. The combinations of AB-PBI, task specific dicationic liquids, MCF, and phosphoric acid will improve the ionic conductivity at higher temperatures, provide higher resistance to impurities, provides good chemical stability, good thermal stability, good mechanical stability. The compositions are easily disposable, environment friendly and do not require any humidification for proton transfer.

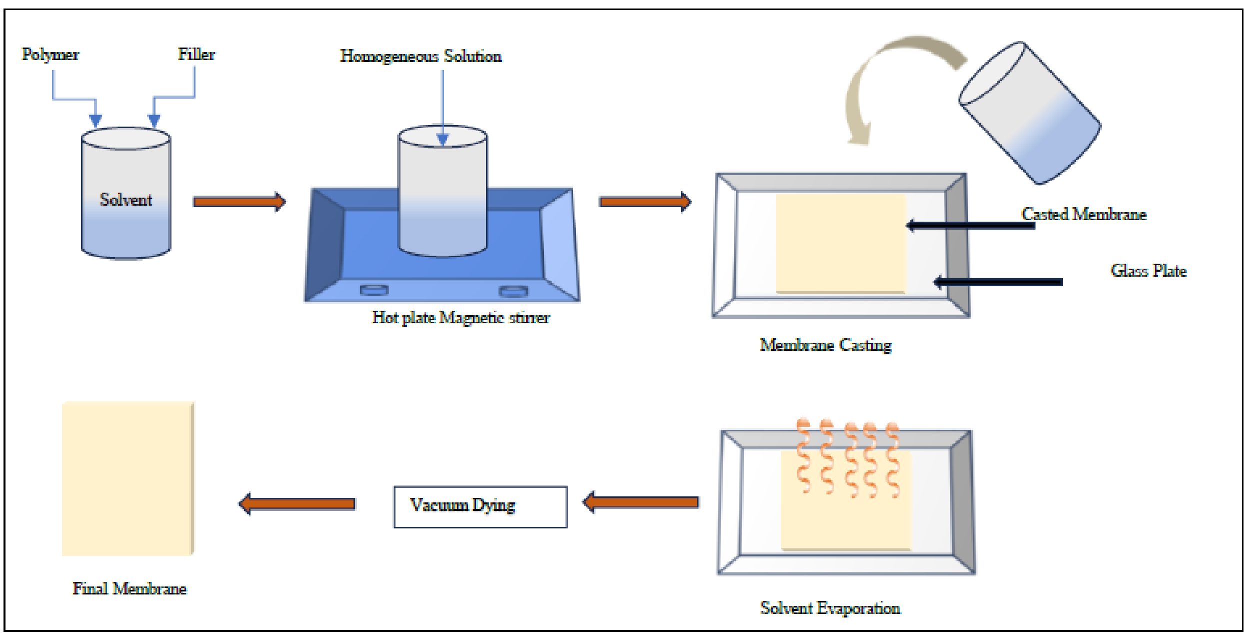

Figure 1

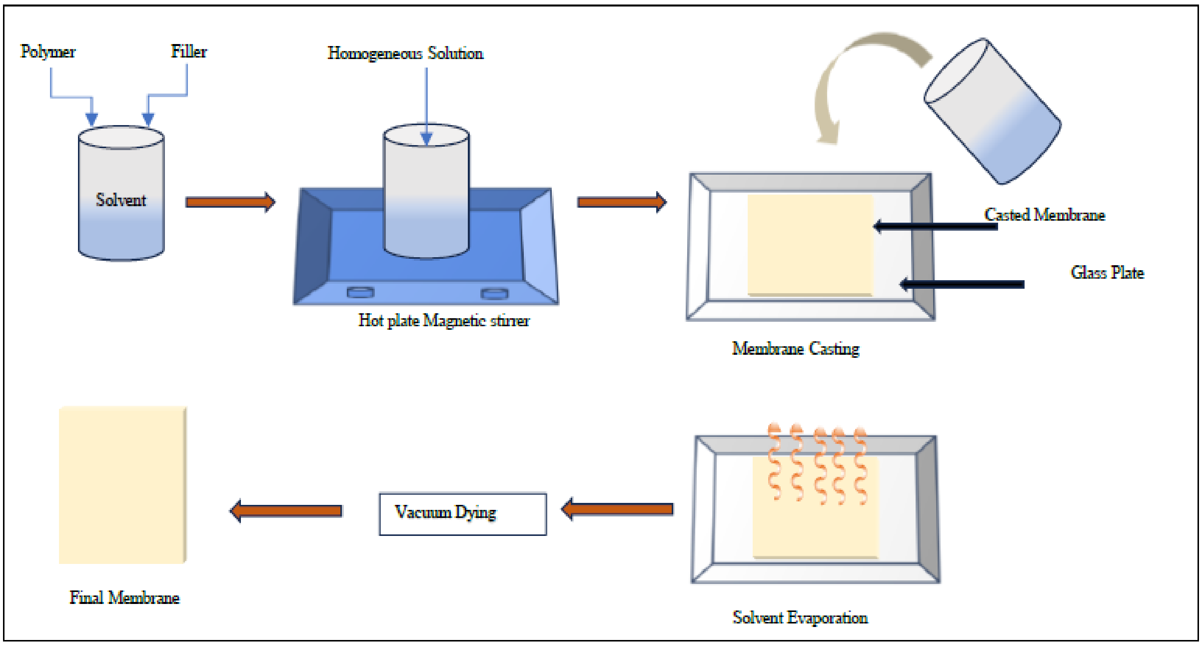

Figure 1

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Bhanu Prasad (INPA No: 3253)
Head, IPR Dept.,
L&T Technology Services Li
DLF 3rd Block, 2nd Floo
Manapakkam, TN, Chennai - 600

Signature Not Verified
Digitally Signed.
Name: Bhanu Prasad
Date: 12-Nov-2024 16:44:22
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