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(54) **PROCEDE DE PRODUCTION DE PATES ET DE GELS DE POLYBENZIMIDAZOLE A UTILISER DANS DES PILES A COMBUSTIBLE**

(54) **PROCESS FOR PRODUCING POLYBENZIMIDAZOLE PASTES AND GELS FOR USE IN FUEL CELLS**

(57) Ce procédé, qui sert à produire une pâte ou un gel de polybenzimidazole (PBI) utiles dans une pile à combustible, consiste à mélanger une poudre polymère de PBI avec une quantité appropriée d'un acide, ce qui amène le polymère à se dissoudre et à former une matrice ayant la consistance d'un gel ou d'une pâte à la température ambiante.

(57) A method for producing polybenzimidazole (PBI) paste or gel useful in a fuel cell, mixing PBI polymer powder with a suitable amount of an acid, which permits the polymer to dissolve and form a matrix having a gel-like or paste-like consistency at room temperature.

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(54) Title: PROCESS FOR PRODUCING POLYBENZIMIDAZOLE PASTES AND GELS FOR USE IN FUEL CELLS

**(57) Abstract**

A method for producing polybenzimidazole (PBI) paste or gel useful in a fuel cell, mixing PBI polymer powder with a suitable amount of an acid, which permits the polymer to dissolve and form a matrix having a gel–like or paste–like consistency at room temperature.

# PROCESS FOR PRODUCING POLYBENZIMIDAZOLE PASTES AND GELS FOR USE IN FUEL CELLS

## Field of the Invention

This invention relates to the manufacture of a paste or gel for use as a polymer electrolyte in fuel cell applications.

## Background of the Invention

Fuel cells can be configured in numerous ways with a variety of electrolytes, fuels and operating temperatures. For example, fuels such as hydrogen or methanol can be provided directly to the fuel cell electrode. Alternatively, fuels, such as methane or methanol, can be converted to a hydrogen rich gas mixture external to the cell itself and subsequently provided to the fuel cell. Air is the source of oxygen in most fuel cells, although in some applications, the oxygen is obtained by hydrogen peroxide decomposition or from a cryogenic storage system.

Although there are theoretically a limitless number of combinations of electrolyte, fuel, oxidant, temperatures and so on, practical systems include solid polymer electrolyte systems using hydrogen or hydrazine as the fuel source and pure oxygen as the oxidant. Polybenzimidazole (PBI) which has been doped with a strong acid is an example of a suitable solid polymer for use in an electrolyte system.

It is known in the art to imbibe polybenzimidazole (PBI) dense films with a strong acid to make a proton conducting media. Particularly, United States Patent

In a further aspect, the present invention provides a polymeric film coated with a PBI paste or gel of the invention.

In a further aspect, the present invention provides a polymeric film coated with a PBI paste or gel of the invention with a second polymeric film forming a sandwich structure.

In still a further aspect, the present invention provides a method for preparing an electrode for use in fuel cells by steps which include coating the electrode with a paste or gel of the invention.

Other aspects and advantages of the present invention are described further in the following detailed description of the preferred embodiments thereof.

## Detailed Description of the Invention

The present invention provides an improvement over the art in methods of preparing a polymeric paste or gel which contains acid and is useful as an electrolyte in fuel cells, particularly chlorine-resistant fuel cells, and in the preparation of adhesives. Also provided are the pastes or gels prepared by the method of the invention, as well as fabric and film coated thereby, and fuel cells containing the pastes or gels of the invention.

Generally, according to the process of the invention, a polymeric paste or gel is prepared by mixing or soaking a polymeric powder with a suitably large amount of an acid solution which causes the polymer to dissolve and form a matrix having a gel-like or paste-like consistency at room temperature. By "suitably large amount of acid" is meant between about

other suitable acid. The present invention is not limited to the choice of suitable acid, provided that the acid swells the polymer, e.g., PBI, and permits the formation of a matrix.

Currently, the most preferred acid solution contains about 85% by weight phosphoric acid and 15% by weight water. However, as stated above, other suitable acid solution concentrations using other selected acids may be readily determined and selected by one of skill in the art.

The polymer and acid solution may be combined and mixed at room temperature. However, any temperature between the freezing point and boiling point of the acid may be used. Optionally, the mixture is heated to enable it to reach a gel-like or paste-like consistency more rapidly than at room temperature. Desirably, the mixture is heated to between about 50°C to about 200°C, and more preferably to between about 100° to about 150°C. Suitably, the heating step is performed for between about five minutes to about four hours, and more preferably for about one hour. Upon cooling, the paste or gel matrix of the invention forms.

Thus, the present invention provides a PBI paste or gel. The resulting PBI paste or gel is characterized by containing between 70 - 99.9% acid, and preferably about 99% acid, by weight. Such a paste or gel is characterized by higher acid loadings and improved electrochemical properties compared to other compositions of the prior art for the same use. For example, the PBI paste or gel of this invention may be characterized by better retention of the acid than the pastes or gels of the prior art (e.g. phosphoric acid and silicon carbide pastes).

*Converting Technology and Equipment*, (D. Satas, ed; Van Nostrand Reinhold) New York (1984). The manner of coating the fabric or film is not a limitation of this invention.

Alternatively, in one particularly desired embodiment, a fabric of the invention is imbibed with acid according to the method described in the co-pending, co-filed US patent application for "Process for Producing Polybenzimidazole Fabrics for Use in Fuel Cells", which is incorporated by reference. Briefly, acid-imbibed fabric disclosed in that application contains between about 40 to about 95% acid, by weight, and more preferably about 50 to about 75% acid, by weight, of the imbibed fabric. A fabric containing polymeric fiber is utilized to prepare the acid-imbibed fabric. Examples of such polymers include, but are not limited to, polybenzimidazole (PBI), poly(pyridine), poly(pyrimidine), polyimidazoles, polybenzthiazoles, polybenzoxazoles, polyoxadiazoles, polyquinoxalines, polythiadiazoles, poly(tetrazapyrenes), and mixtures of sulfonated, non-sulfonated PBI and/or such polymeric fibers. Currently, the preferred fiber is a PBI fiber, which may be either sulfonated or non-sulfonated. Suitable fabrics are readily available from a variety of commercial sources, and are preferably woven and contain voids between the individual fibers in the fabric. However, knitted or non-woven fabrics which contain voids which permit imbibition of the acid, as described herein, may also be utilized. The fabric is imbibed with acid by soaking it in an appropriate acid solution, optionally in the presence of heat. A more detailed description of the acid-imbibed fabric and its

to remove residual water until a consistent paste is obtained. The resulting paste or gel contains about 99% acid by weight.

Example 2

Another exemplary PBI paste is prepared as follows. PBI polymer (5g) was added to a solution containing 112 g 85% $HPO_4$ and 15%, by weight, water in a slow mixer. The mixture is agitated at a temperature of 100-150°C to remove residual water until a consistent paste is obtained. The resulting paste or gel contains about 96% acid by weight.

Example 3

PBI gel prepared from Example 1 was slot-coated at room temperature onto a phosphoric acid imbibed PBI fabric. The thickness of the coating was about 25 μm. A similar coating was applied to a platinum electrode. A membrane electrode assembly was assembled from these materials and a second electrode such that the layers were ordered electrode/gel/fabric/gel/electrode.

Example 4

The membrane electrode assembly fashioned in Example 3 was then placed in a fuel cell. Under typical operating conditions at 0.7 volts the resulting current density and power density is approximately 450 milliamperes/$cm^2$ and 315 milliwatts/$cm^2$, respectively.

Numerous modifications and variations of the present invention are included in the above-identified specification and are expected to be obvious to one of skill in the art. Such modifications and alterations to the compositions and processes of the present

WHAT IS CLAIMED IS:

1. A method for producing a polybenzimidazole (PBI) paste or gel comprising mixing a polymeric PBI powder with a suitable amount of a solution comprising an acid, which permits the polymer to dissolve and form a matrix having a gel-like or paste-like consistency at room temperature.

2. The method according to claim 1, further comprising heating said mixture.

3. The method according to claim 1, wherein said solution further comprises a solvent selected from the group consisting of water and methanol.

4. The method according to claim 3, wherein said acid is present in solution at between 5% by weight to about 100% by weight of said solution.

5. The method according to claim 4, wherein said solvent is present in said solution at between about 0 and about 5% by weight of said solution.

6. The method according to claim 1, wherein said acid is selected from the group consisting of phosphoric acid, acetic acid, formic acid, nitric acid, hydrochloric acid, sulfuric acid, methanesulfonic acid, trifluoroacetic acid, triflic acid and mixtures thereof.

7. The method according to claim 3, wherein the acid is about 70 to about 99.9% of the total weight of said paste or gel.

8. The method according to claim 7, wherein the acid comprises about 95 to about 99% of the total weight of said paste or gel.

AMENDED SHEET

9. The method according to claim 7, wherein the amount of said PBI in said paste or gel is between about 0.1% to about 30% by weight of said paste or gel mixture.

10. The method according to claim 2 wherein said mixture is heated to between about 50 to 200°C for a time sufficient for the mixture to form a paste or gel.

11. The method according to claim 2 wherein said time is between 5 minutes to 4 hours.

12. A polybenzimidazole (PBI) paste or gel comprising a phosphoric acid content of between about 70 to 99.9% by weight and about 0.01 to about 30% by weight, PBI powder, of the total weight of said paste or gel.

13. A PBI paste or gel produced according to any of claims 1 to11.

14. A fuel cell comprising a paste or gel, wherein the paste or gel comprises a phosphoric acid content of between about 70 to 99.9% by weight and about 0.01 to about 30% by weight, polybenzimidazole (PBI) powder, of the total weight of said paste or gel.

15. A polymeric fabric or film coated with a paste or gel, wherein said paste or gel comprises a phosphoric acid content of between about 70 to 99.9% by weight and about 0.01 to about 30% by weight, polybenzimidazole (PBI), of the total weight of said paste or gel.

16. The fabric according to claim 15, which has been imbibed with acid prior to coating with said paste or gel.

17. A fuel cell comprising a fabric coated with a paste or gel, which comprises a phosphoric acid content of between about 70 to 99.9% by weight and about 0.01 to about 30% by weight, polybenzimidazole (PBI), of the total weight of said paste or gel.

18. A polymeric film coated with a paste or gel, wherein the paste or gel comprises a phosphoric acid content of between about 70 to 99.9% by weight and about 0.01 to about 30% by weight, polybenzimidazole (PBI), of the total weight of said paste or gel.

19. A method of preparing an electrode for use in fuel cells comprising coating said electrode with a paste or gel which comprises a phosphoric acid content of between about 70 to 99.9% by weight and about 0.01 to about 30% by weight, polybenzimidazole (PBI), of the total weight of said paste or gel.