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(54) **PROCEDE DE FABRICATION DE COMPOSANTS DE CELLULES ELECTROCHIMIQUES**

(54) **PROCESS FOR THE FABRICATION OF ELECTROCHEMICAL CELL COMPONENTS**

(57) Cette invention se rapporte à un procédé de fabrication d'un composant de cellule électrochimique, comportant une membrane échangeuse d'ions assemblée à un élément de bâti formé dans un matériau polymère dissemblable. Ledit procédé consiste (i) à enduire la bordure d'au moins une face de la membrane échangeuse d'ions, d'une solution dans un solvant miscible avec l'eau du matériau polymère dont est constitué ledit élément de bâti, ou d'un matériau polymère qui est compatible avec le matériau polymère du bâti; (ii) à éventuellement laisser reposer ladite membrane enduite et/ou à la sécher; (iii) à placer la face enduite de la membrane échangeuse d'ions, de l'étape (i) ou de l'étape (ii) en contact avec ledit élément de bâti; et (iv) à assembler la membrane échangeuse d'ions enduite audit élément de bâti.

(57) A process for the fabrication of an electrochemical cell component which comprises an ion exchange membrane joined to a frame member formed from a dissimilar polymeric material, which process comprises the steps of: i) coating the border of at least one face of an ion exchange membrane with a solution in a solvent which is miscible with water of the polymeric material from which the said frame member is made, or of a polymeric material which is compatible with the polymeric frame material; ii) optionally allowing the said coated membrane to stand and/or drying the said coated membrane; iii) placing the coated face of the ion exchange membrane from step (i) or step (ii) in contact with the said frame member; and iv) joining the coated ion-exchange membrane to the said frame member.

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(54) Title: PROCESS FOR THE FABRICATION OF ELECTROCHEMICAL CELL COMPONENTS

(57) Abstract

A process for the fabrication of an electrochemical cell component which comprises an ion exchange membrane joined to a frame member formed from a dissimilar polymeric material, which process comprises the steps of: i) coating the border of at least one face of an ion exchange membrane with a solution in a solvent which is miscible with water of the polymeric material from which the said frame member is made, or of a polymeric material which is compatible with the polymeric frame material; ii) optionally allowing the said coated membrane to stand and/or drying the said coated membrane; iii) placing the coated face of the ion exchange membrane from step (i) or step (ii) in contact with the said frame member; and iv) joining the coated ion-exchange membrane to the said frame member.

PROCESS FOR THE FABRICATION OF ELECTROCHEMICAL CELL COMPONENTS

The present invention relates to a process for the fabrication of electrochemical cell components and, in particular, to a process for joining a membrane to a frame, the said membrane constituting a component of an electrochemical cell such as a fuel cell or a cell for energy storage and/or power delivery.

Ion exchange membranes have been proposed for use in various electrochemical applications, including chlor-alkali cells, fuel cells and energy storage/ power delivery devices. In these devices the ion exchange membrane serves to separate the compartments of the cell, whilst providing a conducting pathway for ions through the cell.

Ion exchange membranes for use in such electrolytic cells may be films of fluoropolymers containing acidic groups or derivatives of acidic groups. Examples of cation exchange membranes are Nafion (DuPont), Flemion (Asahi Glass) and Aciplex (Asahi Chemical). An example of an anion exchange membrane is Tosflex (Tosoh Corporation).

When incorporating ion exchange membranes into electrochemical cells it is important for the membrane to be located in the cell in such a manner that a good joint is formed, to ensure that the membrane becomes an integral part of a membrane frame electrode assembly. Industrial electrolytic or galvanic cells, such as secondary batteries, fuel cells and electrolysers, typically consist of modules which each comprise a number of stacked, layered components which are clamped together in a stack. For example, in a secondary battery of the redox flow type the

components typically consist of electrically insulating flow-frames, each containing an electrode, with a plurality of such flow-frames being sandwiched together with other components such as membranes and meshes. The membranes are generally laid in the wet swelled form between the other components and some membranes have a tendency to tear, crease, fold or puncture as the stack of components is being assembled. An improved method of incorporating the membrane into the cell, which also provides support to the membrane during cell assembly, is required.

Whilst it would be advantageous to join the membrane to a surrounding frame member, in order to assist in the location of the membrane in the cell and to facilitate cell construction, the materials from which ion exchange membranes are formed are not generally readily joinable to a frame member by conventional techniques, such as by welding, since the polymeric material of the membrane will generally be hydrophilic and the polymeric material of the frame member will generally be hydrophobic. We have now developed a process for joining a membrane to a frame member which overcomes these problems.

Accordingly, the present invention provides a process for the fabrication of an electrochemical cell component which comprises an ion exchange membrane joined to a frame member formed from a dissimilar polymeric material, which process comprises the steps of:

i) coating the border of at least one face of a water-containing ion exchange membrane with a solution in a water-miscible solvent of the polymeric material from which the said frame member is made, or of a polymeric material which is compatible with the

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polymeric frame material;

ii) optionally allowing the said coated membrane to stand and/or drying the said coated membrane;

iii) placing the coated face of the ion exchange membrane from step (i) or step (ii) in contact with the said frame member; and

iv) joining the coated ion exchange membrane to the said frame member.

In carrying out the process of the present invention a coating solution is prepared of a polymeric material in a solvent which is miscible with water. The polymeric material is either the same material as that from which the frame is made, or a polymeric material which is compatible therewith. Preferred materials for the construction of the frame are poly(vinylidene fluoride), poly(vinyl chloride), polyurethane or poly(methyl methacrylate). These are therefore the polymers of choice for the formation of the coating solution.

The solvent for the formation of the coating solution is a solvent which is miscible with water. It will be understood that the term "miscible" is intended to include within its scope solvents which are partially or fully miscible with water. This is because the ion exchange membranes contain water and by choosing a solvent for the coating solution which is miscible with water the coating solution is able to impregnate the membrane.

Solvents which are miscible with water are polar solvents such as methanol, ethanol, dimethyl formamide, dimethylsulfoxide, tetrahydrofuran or N-methyl-pyrrolidone.

The coating solution is coated onto the border of at least one face of the ion exchange membrane by

conventional techniques such as roller coating, K-bar coating, painting or screen printing. The particular choice of coating method is not critical to the present invention, providing that an even coating around the border of the membrane can be achieved. It may be advantageous to mask the area of the membrane which is not to be coated since this provides dimensional stability to the membrane.

The concentration of the polymeric material dissolved in the solvent will generally be in the range of from 0.2 to 20% weight by volume of the solvent, preferably 2 to 5% by weight of volume of the solvent.

The ion exchange membrane which is coated in accordance with the present invention may be a fluoropolymer containing acidic groups or derivatives of acid groups. For example, ion exchange membranes which may be used are the copolymers of tetrafluoroethylene and a sulfonated or carboxylated vinyl ether such as those sold under the trade names of Nafion (DuPont), such as Nafion 112, 115 or 117, or Flemion (Asahi Glass). Another perfluorinated cation exchange membrane which may be used in the present invention is Aciplex (Asahi Chemical). Another membrane which may be modified according to the invention is a cation exchange membrane which is a polystyrene sulfonate membrane from Tokuyama Soda sold as Neosepta CM1, Neosepta CM2, Neosepta CMH, Neosepta CMX and Neosepta CMS, and Selemion (Asahi Glass).

Other membranes which may be used in the present invention are heterogeneous membranes such as those based on polystyrene sulfonate ion exchange resin blended with another polymer such as polyethylene. Another type of membrane which may be used is a post-irradiation grafted membrane. An example of an anion

exchange membrane which may be used in the present invention is Tosflex (Tosflex Corporation).

The ion exchange membrane which is used in the present invention will generally have a thickness in the range of from 25 to 250μm, more preferably from 50 to 125μm.

The membrane coated around its border in step (i) of the process of the present invention is preferably allowed to stand or dried before it is joined to the frame member. When the coated membrane is allowed to stand it is believed that beneficial effects may be achieved by the solvent percolating into the pores of the membrane, or by the solvent softening the surface of the frame. When the coated membrane is dried, the drying may either be carried out at room temperature, or by heating as required.

The coated face of the membrane is then contacted with the frame member and the assembly joined together, generally using a combination of heat and pressure to achieve satisfactory joints. The assembly is preferably heated to a temperature at or above the melting point of the polymeric material of the frame, but below the temperature at which the membrane material degrades, so that the polymer material softens and forms a joint with the membrane material. For example, for joining poly(vinylidene fluoride) to Nafion the temperature range will generally be in the range of from about 170°C to 300°C. Suitable techniques for achieving joints between the membrane and the frame member include induction welding, hot bar welding, hot gas welding or ultrasonic welding.

A particular advantage which is associated with the present invention is that the edges of the membrane are heat sealed during the processing steps and this prevents the membrane wicking, which has been

a problem in the past.

The frame/membrane assembly which is produced according to the process of the present invention makes it easier to handle the membrane and provides an easy way of locating the membrane in a cell structure of the type as discussed above. The present invention thus includes within its scope a frame/membrane assembly produced according to the process of the invention.

The present invention also includes within its scope an electrochemical cell which comprises one or more frame/membrane assemblies produced according to the process of the invention.

The present invention will be further described with reference to the following Examples.

EXAMPLE 1

Strips of membrane material (Du Pont's Nafion 117) 25mm wide and approximately 60mm long, were dried under vacuum at 60°C for 30 minutes to remove water from the membrane. Solutions comprising 1g or 2g poly(vinylidene fluoride) dissolved in 40cc of N-methyl-pyrrolidone (NMP) were prepared. Each solution was then applied to the freshly dried membrane by dipping. The coated membranes were then allowed to stand in air. The membranes coated with PVDF were then joined to a poly(vinylidene fluoride) frame using induction heating in the following way. A loop of stainless steel wire was fixed to a ceramic insulator in close proximity to an induction workcoil connected to a high frequency (approximately 180 kHz) power supply. The workcoil heated the stainless steel wire to a temperature of approximately 200°C and this heated the membrane samples and frame materials,

causing a joint to form after approximately 30 seconds.

The joints formed in this way and tested manually were generally weak in peel but relatively strong in tensile. Three specimen joints were immersed in water for over three weeks and then manually tested. The mechanical properties of these joints were unchanged compared to joints tested immediately after joining.

EXAMPLE 2

Following the procedure of Example 1, a solution of 2g of poly(vinylidene fluoride) in 40cc of NMP was applied to Nafion 117 (DuPont). The coated membrane was then allowed to stand.

The membrane was then joined to a PVDF frame using a 3mm wide hot bar weld at 260°C at a pressure of 48.2kPa (7psi) for 3 seconds. A good join was produced.

EXAMPLE 3

Following the procedure of Example 1, a Nafion 115 membrane was dipped in a solution comprising 1g of poly(vinyl chloride) dissolved at room temperature in 20cc tetrahydrofuran.

The membrane was then joined to a PVC frame using a 3mm wide hot bar weld at 175°C at a pressure of 68.9 kPa (10psi) for 5 seconds. A good join was produced.

A similar good join was obtained using a bar temperature of 210°C at a pressure of 7psi for 3 seconds.

EXAMPLES 4 to 28

Strips of membrane (Nafion 117 or 115) were prepared 25mm wide and approximately 60mm long in the as-received state. Solutions comprising 1g or 2g of polymeric material dissolved in 40cc of solvent were prepared. Each solution was applied to the membrane by brushing as a polymeric layer. The membranes coated with the polymeric layer were then joined to polymeric frame materials in the following way. A 3mm wide strip of nichrome electrically resistive tape was protected by a PTFE sheet to prevent sticking, and heated to the temperature indicated. This heated the membrane samples and frame materials, causing a joint to form after the time indicated.

The results obtained are given in the following Table 1.

TABLE 1

Ex. No.	Substrate	Solvent	Polymeric layer	Welding			Comments
				Temp (°C)	Pressure kPa	Time (Sec)	
4	PVDF 1000HD	NMP	PVDF 6000HD 2g in 40ml	245 max	310	10.5	N117 and substrate coated one side and brought together immediately and left overnight. Fair join
5	PVDF 1000HD	NMP	PVDF 6000HD 2g in 40ml	245 max	310	10.5	N117 and substrate coated one side and brought together immediately and left overnight under pressure of about 34 kPa. Fair join
6	PVDF 1000HD	NMP	PVDF 6000HD 2g in 40ml	245 max	310	10.5	N117 coated both sides dry > 10 min. Substrate not coated. Good join
7	PVDF 6000HD	NMP	PVDF 6000HD 2g in 40ml	245 max	310	10.5	N117 coated both sides, substrate one side, dry > 10 mins. Good join
8	PVDF 6000HD	NMP	PVDF 6000HD 2g in 40ml	245 max	310	10.5	N117 and substrate coated one side and brought together immediately. Good join
9	PVDF 1000HD	NMP	PVDF 1000HD 1g in 40ml not fully dissolved	245 max	310	10.5	N117 coated both sides, substrate coated one side, dry >10 mins. Good join
10	PVDF 1000HD	NMP	PVDF 1000HD 1g in 40ml not fully dissolved	245 max	310	10.5	N117 and substrate coated one side and brought together immediately. Good join

TABLE 1 Continued

Ex. No.	Substrate	Solvent	Polymeric layer	Welding			
				Temp (°C)	Pressure kPa	Time (Sec)	Comments
11	PVDF 6000HD	NMP	PVDF 1000HD 1g in 40ml not fully dissolved	245 max	310	10.5	N117 coated both sides and substrate coated one side dry 10 min. Substrate coating not dry after 10 minutes wiped dry. Good join
12	PVDF 6000HD	NMP	PVDF 1000HD 1g in 40ml not fully dissolved	245 max	310	10.5	N117 and substrate coated one side and brought together immediately. Good join
13	PVDF 1000HD	NMP	PVDF 1000HD 2g in 40ml not fully dissolved	245 max	310	10.5	N117 coated both sides and substrate one side, dry 10 mins. Substrate coating not dry after 10 mins wiped dry. Good join
14	PVDF 1000HD	NMP	PVDF 6000HD 2g in 40ml not fully dissolved	245 max	310	10.5	N117 and substrate coated one side and brought together immediately. Good join
15	PVDF 6000HD	NMP	PVDF 1000HD 2g in 40ml not fully dissolved	245 max	310	10.5	N117 coated both sides and substrate coated one side dry 10 mins. Substrate coating not dry after 10 mins wiped dry. Good join

TABLE 1 Continued

Ex. No.	Substrate	Solvent	Polymeric layer	Welding			
				Temp (°C)	Pressure kPa	Time (Sec)	Comments
16	PVDF 6000HD	NMP	PVDF 1000HD 2g in 40ml not fully dissolved	245 max	310	10.5	N117 and substrate coated one side and brought together immediately. Good join
17	PMMA Diakon®	NMP	PVDF 6000HD 2g in 40ml	245 max	310	10.5	N117 and substrate coated one side and brought together immediately dry overnight. Good join
18	PMMA Diakon®	NMP	PVDF 6000HD 2g in 40ml	245 max	310	10.5	N117 and substrate coated one side and brought together immediately dry overnight under pressure of about 34 kPa. Good join
19	PU Davathane®	THF	PU Davathane® 1g in 20ml	205 max	310	7	N117 coated both sides and substrate one side, air dried > 10 mins. Good join
20	UPVC EDP	THF	UPVC EDP 1g in 20ml	205 max	310	7	N117 coated both sides and substrate one side brought together after 1 min leave 25 min. Good join
21	PU Davathane®	THF	PU Davathane® 1g in 20ml	115 max and 205 max	45	3.5 & 7	N117 coated both sides and substrate one side, brought together after 1 min allowed to dry 30 min. Good join
22	PU Davathane®	THF	PU Davathane® 1g in 20ml	205 max	45	7	N117 coated both sides and substrate one side, air dried > 10 min. Good join

TABLE 1 Continued

Ex. No.	Substrate	Solvent	Polymeric layer	Welding			
				Temp (°C)	Pressure kPa	Time (Sec)	Comments
23	PVDF 1000HD	NMP	Kynar Flex 2851-00 PVDF/HFP Coplymer 1g in 20ml	245 max	310	10.5	N115 and substrate coated on one side and brought together immediately leave for > 10 mins, Good join
24	PVDF 6000HD	NMP	Kynar Flex 2851-00 PVDF/HFP Copolymer 1g in 20ml	245 max	310	10.5	N115 and substrate coated one side and brought together immediately leave for > 10 min. Good join
25	PVDF 1000HD	DCM	PMMA Diakon® 1g in 20ml	245 max	310	10.5	N115 and substrate coated one side and brought together immediately leave for > 10 min. Good join
26	PVDF 6000HD	DCM	PMMA Diakon® 1g in 20ml	245 max	310	10.5	N115 and substrate coated one side and brought together immediately leave for > 10 min. Good join
27	PVDF 1000HD	NMP	Kynar Flex 2851-00 PVDF/HFP Copolymer 1g in 20ml	245 max	310	10.5	N117 and substrate coated one side and brought together immediately leave for > 10 min. Good join

TABLE 1 Continued

Ex. No.	Substrate	Solvent	Polymeric layer	Welding			
				Temp (°C)	Pressure kPa	Time (Sec)	Comments
28	PVDF 6000HD	NMP	Kynar Flex 2851-00 PVDF/HFP Copolymer 1g in 20ml	245 max	310	10.5	N117 and substrate coated one side and brought together immediately leave for > 10 mins, Fair join

Footnotes to the Table:

NMP	-	N-methyl-pyrrolidone
THF	-	tetrahydrofuran
DCM	-	dichloromethane
PVDF	-	poly(vinylidene fluoride)
PVDF	-	1000 HD (Elf Atochem)
	-	6000 HD (Elf Atochem)
PU	-	polyurethane
UPVC	-	poly(vinyl chloride)
PMMA	-	poly(methyl methacrylate)
EDP	-	Engineering Design Plastics "Palclear"
PVDF/HFP	-	poly(vinylidene fluoride)/hexafluoropropylene Copolymer

CLAIMS:

1. A process for the fabrication of an electrochemical cell component which comprises a water-containing ion exchange membrane joined to a frame member formed from a dissimilar polymeric material, which process comprises the steps of:

i) coating the border of at least one face of a water-containing ion exchange membrane with a solution in a water-miscible solvent of the polymeric material from which the said frame member is made, or of a polymeric material which is compatible with the polymeric frame material;

ii) optionally allowing the said coated membrane to stand and/or drying the said coated membrane;

iii) placing the coated face of the ion exchange membrane from step (i) or step (ii) in contact with the said frame member; and

iv) joining the coated ion-exchange membrane to the said frame member.

2. A process as claimed in claim 1 wherein the frame member is made from poly(vinylidene fluoride) or poly(vinyl chloride), polyurethane or poly(methyl methacrylate).

3. A process as claimed in claim 1 or claim 2 wherein the solvent in which the polymeric material is dissolved or dispersed is methanol, ethanol, dimethyl formamide, dimethylsulfoxide, tetrahydrofuran or N-methyl-pyrrolidone.

4. A process as claimed in any one of the

preceding claims wherein the membrane is coated by roller coating, K-bar coating, painting or screen printing.

5. A process as claimed in any one of the preceding claims wherein the membrane is a cation exchange membrane.

6. A process as claimed in claim 5 wherein the cation exchange membrane is a copolymer of tetrafluoroethylene and a sulfonated or carboxylated vinyl ether.

7. A process as claimed in claim 5 or claim 6 wherein the membrane has a thickness in the range of from 50 to 125μm.

8. A process as claimed in any one of the preceding claims wherein the coated membrane is dried in step (ii) using heat.

9. A process as claimed in any one of the preceding claims wherein the coated membrane is joined to the frame using heat and pressure.

10. A process as claimed in claim 9 wherein the joining of the membrane to the frame is carried out at a temperature at or above the melting point of the frame material.

11. A frame/membrane assembly which has been produced by a process as claimed in any one of the preceding claims.

12. An electrochemical cell which comprises one

or more frame/membrane assemblies as claimed in claim 11.