Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2341495 C 2010/07/06

(11)(21) **2 341 495**

(12) **BREVET CANADIEN**
CANADIAN PATENT

(13) **C**

---

(86) Date de dépôt PCT/PCT Filing Date: 1999/08/20

(87) Date publication PCT/PCT Publication Date: 2000/03/09

(45) Date de délivrance/Issue Date: 2010/07/06

(85) Entrée phase nationale/National Entry: 2001/02/23

(86) N° demande PCT/PCT Application No.: DE 1999/002622

(87) N° publication PCT/PCT Publication No.: 2000/013243

(30) Priorité/Priority: 1998/08/26 (DE198 38 786.5)

(51) Cl.Int./Int.Cl. *H01M 4/86* (2006.01),
H01M 4/88 (2006.01), *H01M 8/10* (2006.01),
H01M 4/92 (2006.01)

(72) Inventeurs/Inventors:
DATZ, ARMIN, DE;
SCHRICKER, BARBARA, DE;
WAIDHAS, MANFRED, DE

(73) Propriétaire/Owner:
SIEMENS AKTIENGESELLSCHAFT, DE

(74) Agent: SMART & BIGGAR

---

(54) Titre : ELECTRODE DE DIFFUSION DE GAZ ET METHODE DPRODUCTION
(54) Title: GAS DIFFUSION ELECTRODE AND METHOD FOR ITS PRODUCTION

(57) Abrégé/Abstract:

Improved gas diffusion electrode, method of producing said electrode and method of hydrophobicizing a gas diffusion electrode The invention relates to an improved gas diffusion electrode for use in PEM fuel cells, a method for its production and a method of hydrophobicizing a gas diffusion electrode. The electrocatalyst layer of the improved gas diffusion electrode has a significantly lower content of the catalyst inhibitor Teflon, since the Teflon is not added only to the screen-printing paste as hitherto but subsequently applied, with the same surface-specific effect, by dipping the finished electrocatalyst layer in a solution containing Teflon.

GR 98 P 8088 PCT1

Abstract

Improved gas diffusion electrode, method of producing said electrode and method of hydrophobicizing a gas diffusion electrode

The invention relates to an improved gas diffusion electrode for use in PEM fuel cells, a method for its production and a method of hydrophobicizing a gas diffusion electrode. The electrocatalyst layer of the improved gas diffusion electrode has a significantly lower content of the catalyst inhibitor Teflon, since the Teflon is not added only to the screen-printing paste as hitherto but subsequently applied, with the same surface-specific effect, by dipping the finished electrocatalyst layer in a solution containing Teflon.

Description

Gas diffusion electrode and method for its production

The invention relates to a gas diffusion electrode for use in PEM fuel cells and to a method for its production, as specified in the preambles of the independent claims. The production method is intended in particular to make hydrophobicization of the gas diffusion electrode possible.

The core of a PEM fuel cell is a membrane electrode unit, which is built up from a membrane with an electrode that is coated on both sides and comprises an electrocatalyst layer. The electrode normally has a solid, gas-permeable and electrically conductive carrier (e.g. carbon fabric or carbon paper), which is preferably hydrophobicized with a polymer suspension (in the following text, the polymer will be called polymer A, which here concerns polymers such as PTFE, i.e. polytetrafluoroethylene, Teflon). Applied to this carrier is an electrocatalyst layer which, in turn, is again hydrophobicized. The polymer A can therefore be contained both in the carrier and in the electrocatalyst layer. In addition, the electrode can contain a further polymer as binder which, in the present connection, is designated polymer B.

The necessary content of polymer A for hydrophobicizing the electrocatalyst layer has previously generally been 20-60% by weight, a higher content of polymer A, such as Teflon, inhibiting the activity of the platinum catalyst, increasing the content resistance and reducing the porosity of the electrode (Watanabe, J. Elektroanal. Chem. 195 (1985) 81-83), that is to say has a detrimental effect on the system. The polymer A for hydrophobicizing the electrocatalyst layer can therefore also be referred to as a "catalyst inhibitor".

In the electrode known hitherto, in addition to a high content of polymer A for hydrophobicizing the electrocatalyst layer (20-60% by weight, always based on the content of metallic catalyst), the homogeneity of the thickness of the electrocatalyst layer also presents a problem. There is a requirement to provide a suitable production method which, cost-effectively and capable of mass production, permits a uniform coating of the carrier with dry catalyst powder in low layer thicknesses of 3-40 µm.

According to the conventional methods (Watanabe, J. Electroanal. Chem. 195 (1985) 81-83; J. Elektroanal. Chem. 197 (1986) 195-208 M. Uchida, J. Elektrochem. Soc., 142 (1995) 463-468), a dry powdered mixture of catalyst powder previously hyrophobicized with PTFE is pressed onto the likewise hydrophobicized carrier. In order to product the mixture, firstly the carbon powder is mixed intensively with PTFE dispersion and then dried at a temperature above 280°C. In the process, the surface-active wetting agent (Triton* X 100) contained in the dispersion is removed. The wetting agent is used to compensate for the poor processing properties which arise from the high content of polymer A in the screen-printing paste. The mixture is then pulverized, this method is very complicated, and a uniform thickness of the electrocatalyst layer in low layer thicknesses may be produced technically only with great difficulty and in low numbers. In addition, the disadvantage with this method is that

- a high content of polymer A for hydrophobicizing the electrocatalyst layer is contained, and
- for the purpose of processing, a wetting agent is added, which has to be removed specifically and leaves behind interfering residues.

*Trade-mark

The prior art discloses gas diffusion electrodes for use in electrochemical cells, for example from US 4,568,442 A and US 4,615,954 A. In this case, the surface of such a gas diffusion electrode is to be hydrophobic, a polymer proportion of 30% being viewed as suitable, in particular in an example in US 4,615,954 A.

According to US 4,229,490 A and EP 0 357 077 A1, the production of such gas diffusion electrodes is carried out by the screen-printing technique. Screen printing is a known technique for producing a uniformly thin layer. The use of screen printing to build up an electrochemical system is already known. According to US 4,229,290 A, for this purpose the screen-printing paste, which contains Teflon* dispersion, graphite and platinum black, must in turn have added to it more than 50% by weight of the wetting or dispersing agent "Triton* X 100" for the purpose of stabilization. The proportion of Teflon* used for hydrophobicization in the screen-printing paste, and therefore that present in the resulting electrocatalyst layer, is about 25% by weight. The paste is printed onto a solid carrier, for example carbon paper, which again contains 60% by weight of Teflon*. The result is a total content of Teflon* of about 85%. The drawback with the electrode produced by this method, in addition to the extremely high content of polymer A for hydrophobicizing the electrocatalyst layer (here: Teflon*), is also the wetting agent added to more than 50% by weight (of the catalyst paste).

On the basis of the prior art, it is an object of the invention to provide an improved gas diffusion electrode and to specify a method for its production. The production method should be cost-effective and capable of mass production, and achieve the hydrophobicization of the gas diffusion electrode with a low proportion of polymer.

*Trade-mark

The subject of the invention is a gas diffusion electrode for a PEM fuel cell having an electrocatalyst layer which has a content of hydrophobicizing polymer A of less than 10% by weight and a uniform thickness of the electrocatalyst layer of less than or equal to 20 µm. Also subject of the invention is a gas diffusion electrode which is produced by a screen-printing process with a screen-printing paste which comprises a content of polymer A for hydrophobicizing the electrocatalyst layer of at most 10% (based on the content of metallic catalyst), at least one metallic catalyst and a high-boiling solvent. Finally, a further subject of the invention is a method for producing a gas diffusion electrode in which, in the screen-printing process, a catalyst paste which contains at least one metallic catalyst and a screen-printing medium is printed onto an electrode and/or a membrane, and the screen-printing medium is removed by heating in a following, second operation. Finally, a further subject of the invention is a method for hydrophobicizing a gas diffusion electrode, in which a ready-coated electrode is dipped into a solution of the polymer A for the purpose of hydrophobicization. A use of a gas diffusion electrode according to the invention in a fuel cell is also a subject of the invention.

Thus, in accordance with one aspect of the invention, there is provided a gas diffusion electrode for a PEM fuel cell, having an electrocatalyst layer which has a content of polymer A for hydrophobicizing the electrocatalyst layer of less than 10% by weight, based on the content of metallic catalyst, and a uniform thickness of the electrocatalyst layer of less than or equal to 20 μm.

In accordance with another aspect of the invention, there is provided a method of producing the gas diffusion electrode as described herein, carrying out a screen-printing process with the following operations: in a first operation of the screen-printing process, a screen-printing paste, which comprises at least one metallic catalyst with a content of polymer A of up to 10% and a screen-printing medium, is printed onto a carrier, and in a second operation, the screen-printing medium is removed by heating.

In accordance with another aspect of the invention, there is provided the use of the gas diffusion electrode as described herein, produced as described herein, in a fuel cell.

According to an advantageous embodiment of the invention, the electrocatalyst conveyor and/or the screen-printing paste (based on their content of metallic catalyst) contain only 0.01 to 1% by weight, preferably 0.05 to 0.5% by weight and particularly preferably 0.075 to 0.2% by weight and in particular 0.1% by weight of polymer A for hydrophobicizing the electrocatalyst layer.

According to an advantageous refinement of the invention, the polymer A for hydrophobicizing the electrocatalyst layer is Teflon, in particular an amorphous modification of Teflon which can be brought into solution.

The metallic catalyst used is preferably platinum black or platinum on carbon.

The high-boiling solvent used in the screen-printing and/or catalyst paste is preferably an ester and/or a ketone and/or an alcohol, particularly preferably glycolic acid butyl ester, cyclohexanone and/or terpineol.

According to one refinement of the invention, the catalyst paste, apart from the metallic catalyst and the high-boiling solvent, also has added to it as binder a polymer B, preferably a polymer which can be baked out to 400°C.

In one embodiment of the gas diffusion electrode, the content of the polymer A in the electrocatalyst layer for hydrophobicizing the electrocatalyst layer approaches zero, zero being ruled out.

According to one embodiment of the method, in which, for example, the polymer A can be omitted completely from the screen-printing paste, the hydrophobicization of the finished electrocatalyst layer is carried out after the screen-printing coating by dipping the complete electrode into a solution of the hydrophobicizing polymer A. The solution contains the polymer A preferably at 0.01 to 1% by weight, particularly preferably 0.05 to 0.5% by weight and quite particularly preferably 0.075 to 0.2% by weight, in particular 0.1% by weight. The solvent is preferably a perfluorinated solvent like a completely fluorinated organic compound which, for example, can be produced by the electrochemical fluorination of alkanes.

In this embodiment of the method, it is advantageous if, following the hydrophobicization, the electrode is dried in a further operation, preferably at temperatures between 20°C and 120°C.

In a further modification of the method, in order to fill up the large pores and therefore to reduce the quantity of catalyst needed for complete coating, first of all a carbon paste consisting of electrically conductive carbon black and screen-printing medium is printed onto the carrier. This produces the very first screen-printed coating of the carrier with carbon. Only following the drying of this first screen-printed coating is the screen printing with the - considerably more expensive - catalyst paste carried out.

According to a further refinement of the method, in order to achieve a different content of polymer A in the gas diffusion electrode, both the carbon paste of the first screen-printing operation and the carrier, or both, can additionally contain polymer A.

The total content of polymer A in the gas diffusion electrode is conceptually separated from the critical content of "polymer A for hydrophobicizing the electrocatalyst layer", since the designation listed is understood to mean only the quantity of polymer A which is applied to the electrocatalyst layer by the dip bath and/or via the screen-printing paste. The total content of polymer A in the gas diffusion electrode (that is to say the content of polymer A in the carrier, in the first screen-printed layer and in the electrocatalyst layer together) advantageously adds up to up to 20% by weight, preferably to less than 15% by weight and particularly preferably to less than 10% by weight, quite particularly preferably to less than 5% by weight and in particular to less than 3.5% by weight.

The polymer A preferably used is Teflon, in particular a modification which is present in amorphous and/or transparent form and may be dissolved completely in fluorinated solvents. Alternatively, however, a different polymer, such as ethylene propylene copolymer or a different fluorine-containing polymer, e.g. PVDF (polyvinylidene fluoride) can also be used.

The electrocatalyst layer referred to here is the layer which is preferably applied to a solid, gas-permeable and electrically conductive carrier of the electrode, and on whose catalytic surface the anodic oxidation of the fuel to protons or the cathodic reduction of the oxygen takes place. The electrocatalyst layer comprises at least the metallic catalyst, which preferably contains platinum and can be used in pure form as platinum black or in diluted form as platinum on carbon in the catalyst paste. The electrocatalyst layer preferably contains no further constituents since, according to the preferred embodiment of the invention, the screen-printing medium which is added to the catalyst paste for processing has been removed by drying and heating the finished, that is to say coated, electrode.

The "uniform electrocatalyst layer thickness" referred to here is a layer of 3 - 40 μm thickness, which has been applied by a conventional screen-printing process and whose thickness fluctuation are generally below those which can be achieved with a different coating technique for fuel-cell electrodes.

For the purpose of processing, the screen-printing paste (also called carbon or catalyst paste, depending on the operation) has added to it at least a high-boiling solvent as a screen-printing medium, such as an ester, ketone and/or an alcohol, in particular glycolic acid butyl ester, cyclohexanone and/or terpineol. It is advantageous if, as screen-printing medium, it is not only a high-boiling solvent which is added but also, as a binder, a polymer B, such as polyvinyl alcohol and/or polyethylene oxide. The polymer B can preferably be baked out, in particular at temperatures up to 400°C, or leaves behind only residues which do not interfere with the operation of the fuel cell.

The electrode is a gas-permeable, electrically conductive layer on the membrane, which preferably comprises a carrier with an electrocatalyst layer. The carrier or substrate used is preferably a carbon fabric or a carbon paper or another porous and electrically conductive substrate.

In the following text, the method according to the invention will be explained in more detail using a preferred embodiment.

In order to produce the screen-printing pastes, the carbon or catalyst powder is added to a screen-printing medium, consisting of polyethylene oxide dissolved in terpineol, for example, while stirring. The content of binder is 0 to 20% by weight, preferably 5 to 15% by weight. The catalyst used is platinum black or platinum on carbon. Screen printing is carried out with a commercially available screen-printing machine. Stainless-steel screens with a size of up to 760 * 700 mm^2 are used, with a mesh width of 100 to 300 meshes per inch (about 39 to 118 meshes per cm). Using the latter, wet layer thicknesses from 6 to 60 µm per printing operation can be achieved. Virtually any desired areas are coated per printing operation, limited by the size of the printable area of the screen-printing machine. Following the printing operation, the electrodes are dried at 120°C and baked out at 360°C in order to remove the binder.

The platinum covering, determined by weighing, is 2-3 mg/cm^2 if pure platinum black is used as the catalyst, and 0.15 to 0.4 mg/cm^2 if platinum on carbon is used as the catalyst, depending on the platinum covering of the carbon.

For the purpose of hydrophobicization, the ready-coated gas diffusion electrode is dipped into a solution of a polymer A for hydrophobicizing the electrocatalyst layer and then dried. Any desired gas diffusion electrode can be hydrophobicized retrospectively in this way.

Current/voltage curves of membrane/electrode units with gas diffusion electrodes according to the invention were recorded, in which an extremely low voltage drop at high current intensities could be observed. This can be attributed, inter alia, to the low diffusion inhibition, caused by the low content of polymer A and damage to the hydrophobicization by residues of wetting agent within the porous electrocatalyst layer.

The present method by means of screen printing makes it possible to reduce the costs for electrode production considerably. Using the screen-printing process, a uniform layer thickness is achieved over the entire electrode, even in the case of large electrodes (e.g. 36 * 36 cm^2), as well as good reproducibility during mass production. Since the hydrophobicization is carried out only at the conclusion of the method, if at all, by dipping the complete electrode into a solution of the polymer A, the processing properties (and the bake-out behavior) of the screen-printing pastes are not impaired by the polymer suspension and additional wetting and dispersion agents, which tend to coagulation and/or foaming.

According to the invention, in order to hydrophobicize the electrode, considerably lower quantities of polymer A are needed in the electrocatalyst layer, since the polymer A is deposited from the solution only as a thin film on the surface of the electrode particles (carbon, platinum etc.). The electrocatalyst layer advantageously contains only 0.01 to 0.5% by weight, preferably 0.05 to 0.3% by weight and particularly preferably 0.075 to 0.2% by weight, and in particular 0.1% by weight of polymer A for hydrophobicizing the electrocatalyst layer, instead of 20 - 60% by weight as hitherto. As a result, blockage of the gas pores by polymer A agglomerates in the electrocatalyst layer and/or in the carrier are prevented to the maximum extent.

The invention replaces the previous hydrophobicization technique in gas diffusion electrodes of fuel cells. In an embodiment, the ready-coated electrode is dipped into a hydrophobicization bath. The particular advantage of this gas diffusion electrode is, in addition to the low content of polymer A, also the improved homogeneity of the layer thickness, since the electrocatalyst paste can be processed better in the screen-printing process without the addition of polymer A.

CLAIMS:

1. A gas diffusion electrode for a PEM fuel cell, having an electrocatalyst layer which has a content of polymer A for hydrophobicizing the electrocatalyst layer of less than 10% by weight, based on the content of metallic catalyst, and a uniform thickness of the electrocatalyst layer of less than or equal to 20 μm.

2. The gas diffusion electrode as claimed in claim 1, wherein the content of polymer A for hydrophobicizing the electrocatalyst layer is between 0.01 and 1% by weight.

3. The gas diffusion electrode as claimed in claim 2, wherein the content of polymer A in the electrode catalyst layer is at 0.01% by weight.

4. A method of producing the gas diffusion electrode as claimed in any one of claims 1 to 3, carrying out a screen-printing process with the following operations:

- in a first operation of the screen-printing process, a screen-printing paste, which comprises at least one metallic catalyst with a content of polymer A of up to 10% and a screen-printing medium, is printed onto a carrier, and

- in a second operation, the screen-printing medium is removed by heating.

5. The method as claimed in claim 4, wherein the screen-printing medium used is a high-boiling solvent.

6. The method as claimed in claim 4 or claim 5, wherein the second operation involves heating the screen-printing medium to at most 400°C.

7. The method as claimed in any one of claims 4 to 6, wherein the carrier used is a substrate which already contains polymer A.

8. The use of the gas diffusion electrode as claimed in any one of claims 1 to 3, produced as claimed in any one of claims 4 to 7, in a fuel cell.

FETHERSTONHAUGH & CO.
OTTAWA, CANADA

PATENT AGENTS