



(86) Date de dépôt PCT/PCT Filing Date: 2005/07/09
(87) Date publication PCT/PCT Publication Date: 2006/01/26
(45) Date de délivrance/Issue Date: 2012/09/11
(85) Entrée phase nationale/National Entry: 2007/01/11
(86) N° demande PCT/PCT Application No.: EP 2005/007467
(87) N° publication PCT/PCT Publication No.: 2006/008014
(30) Priorité/Priority: 2004/07/19 (DE10 2004 034 885.5)

(51) Cl.Int./Int.Cl. *H01M 4/86* (2006.01),
C25B 11/00 (2006.01), *H01M 4/88* (2006.01),
H01M 4/90 (2006.01)

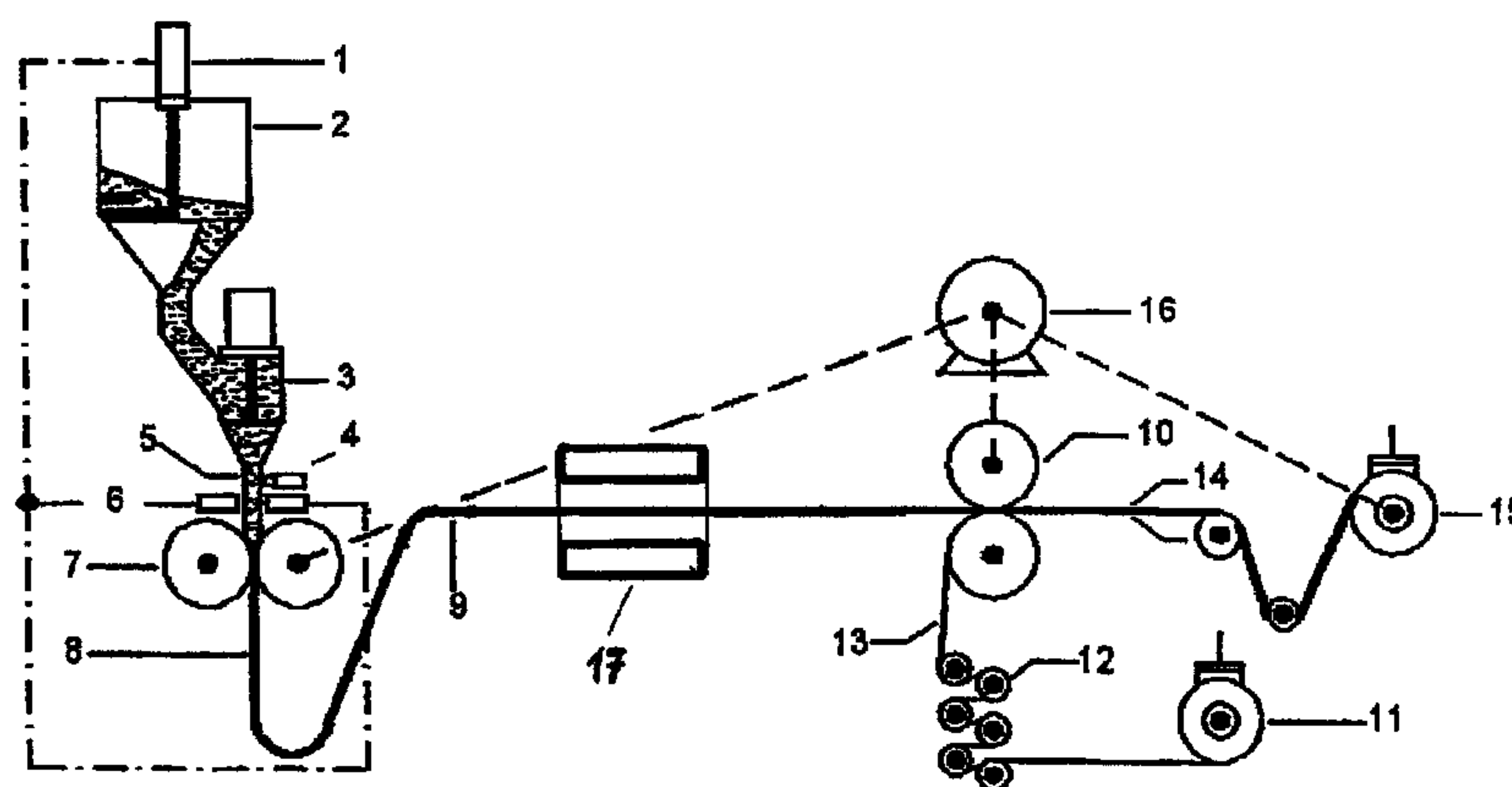
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(54) Titre : ELECTRODE DE DIFFUSION DE GAZ A L'ARGENT EN MILIEU DE DIOXYDE DE CARBONE, ET METHODE DE PRODUCTION

(54) Title: SILVER-GAS DIFFUSION ELECTRODE FOR USE IN AIR CONTAINING CO₂ AND A METHOD FOR PRODUCING THE SAME



(57) Abrégé/Abstract:

The invention relates to a method for the production of a gas diffusion electrode from a silver catalyst on an PTFE-substrate. The pore system of the silver catalyst is filled with a moistening filling agent. A dimensionally stable solid body having a particle size greater than the particle size of the silver catalyst is mixed with the silver catalyst. Said compression-stable mass is formed in a first calendar in order to form a homogenous catalyst band. In a second calendar, an electroconductive discharge material is embossed in the catalyst band, and heating takes places between the first and the second calendar by means of a heating device, wherein at least parts of the moistened filling agent are eliminated. The invention also relates to a gas diffusion electrode which is produced according to said method.

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ABSTRACT

The invention relates to a method for the production of a gas diffusion electrode from a silver catalyst on an PTFE-substrate. The pore system of the silver catalyst is filled with a moistening filling agent. A dimensionally stable solid body having a particle size greater than the particle size of the silver catalyst is mixed with the silver catalyst. Said compression-stable mass is formed in a first calendar in order to form a homogenous catalyst band. In a second calendar, an electroconductive discharge material is embossed in the catalyst band, and heating takes places between the first and the second calendar by means of a heating device, wherein at least parts of the moistened filling agent are eliminated. The invention also relates to a gas diffusion electrode which is produced according to said method.

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Silver-Gas Diffusion Electrode for Use in Air Containing CO₂ and a Method
for Producing the Same

[0001] The present invention relates to an oxygen-consumption electrode in alkaline electrolytes for operation in a mixture of gases that contains CO₂, such as air, and a method for producing such an electrode.

[0002] Alkaline electrolytes have been used as ion conductors in electrochemical process technology for more than 150 years. They mediate the movement of current in alkaline batteries and in alkaline electrolyzers, and in alkaline fuel cells. Some of these systems are hermetically sealed and for this reason do not come into contact with atmospheric oxygen. In contrast to this, other fuel cells, in particular chlorine-alkaline electrolysis and alkaline fuel cells, have to be supplied with atmospheric oxygen. Experiments have shown that operation with impure air that contains CO₂ reduces the operating life of the device.

[0003] A known reaction of the typical alkaline electrolyte potassium hydroxide and sodium hydroxide with the carbon dioxide in the air leads to the formation of carbonates and water:



The carbonate crystallizes out or remains in solution, depending on the pH value of the remaining solution. This is undesirable for a number of reasons:

- Sodium hydroxide, not sodium carbonate, is to be produced in the chlorine-alkali electrolysis. Carbonization reduces the efficiency of the device.
- In alkaline fuel cells, the conductivity of the potassium hydroxide is reduced by formation of potassium carbonate. This is noticeable, in particular, at high current densities, and it has a negative effect on electrical efficiency.
- In the case of zinc/air cells, or even in alkaline fuel cells, the carbonate can crystallize in the pores of the porous gas diffusion electrode and completely block the access of air. This renders the batteries or fuel cells unserviceable.

[0004] For these reasons, it is preferred that systems with alkaline electrolytes be operated not with air, but only with pure oxygen, or that CO₂ filters be integrated in them.. Various filtering methods can be used, depending on the quantity of air throughput. Pressure reversal devices work economically with large volumes of air, whereas a solid filter or a liquid filter will be used for smaller volumes of air.

[0005] The problem of carbonization has been the subject of discussion in the relevant prior art for a considerable time. Alkaline fuel cells (AFC) were extensively researched from 1950 to 1975. During the energy crisis of that time, AFC's were regarded as environmentally friendly and effective energy converters. For that reason, despite the known carbonization, investigations were initiated in order to ascertain the effects of atmospheric carbon dioxide on the efficiency of the cells. The results that were obtained at that time confirmed the theory that operation of alkaline fuel cells using air that had not been purified is not possible over the long term, because the cells failed after a few hundred hours. The core of the problem is the pores of the gas diffusion electrode, which become blocked by carbonates. A summary of these results is to be found in Kordesch, *Hydrocarbon Fuel Cell Technology*, Academic Press, 1965, pp. 17 – 23. In summary, these results indicate that hydrophilic electrodes carbonize more rapidly than hydrophobic electrodes, and that carbonization occurs more rapidly at high than at low voltages.

[0006] A more recent observation has recently been published by Gülzow in *Journal of Power Sources* 127, 1-2, 2004, pp. 243, wherein the enrichment of carbonates in the potassium lye was measured during long-term operation. In contrast to the Kordesch observations, no saturation of the carbonization occurs in this particular case.

[0007] Gas diffusion electrodes (hereinafter GDE) have been used for many years in batteries, electrolyzers, and fuel cells. Electrochemical conversion takes place in these electrodes only at the so-called three-phase boundary. The three-phase boundary is defined as the area in which the gas, the electrolyte, and the metallic conductor meet one another. In order that the GDE operates effectively, the metallic conductor should also be

a catalyst for the desired reaction. Silver, nickel, manganese dioxide, carbon, and platinum, are suitable catalysts among many others. Their surface areas must be large in order that the catalysts are particularly effective. This is achieved by fine powder or porous powder with internal surface.

[0008] The liquid electrolyte is drawn into such fine-pore structures by capillary action. This takes place more or less completely, depending on viscosity, surface tension, and pore radius. However, this capillary action is particularly great in the case of alkaline electrolytes, since potassium hydroxide and sodium hydroxide have a slight wetting effect and viscosity is low at the usual operating temperature of 80°C.

[0009] There are three ways to ensure that the GDE is not completely filled with electrolyte, i.e., in order to ensure easy access for the gas:

- Pores with a diameter of greater than 10 µm are generated; these cannot fill with electrolyte at increased gas pressure (50 mbar).
- Hydrophobic materials are introduced in part into the electrode structure, and hinder the wetting process.
- The surfaces of the catalyst react hydrophobically to the electrolyte to different degrees. In particular, in the case of catalysts that contain carbon, hydrophobicity can be varied by the specific removal of certain surface groups.

[0010] Typically, all ways are implemented in order to fabricate GDE's. The size of the pores can be adjusted by the starting material and by additional pore-forming agents. In addition, production parameters such as pressure and temperature also affect the size of the pores. Hydrophobicity is adjusted by plastic powder—mostly PTFE or PE—and by its percentage of mass and distribution. The hydrophobicity of the catalyst is based on material and its production/processing.

[0011] There are two fundamental methods for fabricating gas diffusion electrodes from mixtures of PTFE and catalyst; they are described in Patents DE 29 41 774 and US 3,297,484. Carbon with applied catalyst is mostly used as catalyst and metallic

conductors. In rare instances, however, pure metal catalysts are used, as described, for example, in WO 03/004726 A2. If the system consists of only one component (pure metal or alloy) and not of a heterogeneous mixture of carbon and metal (carrier catalyst), the wetting characteristics are simpler to adjust at the microscopic level than is the case with carrier catalysts.

[0012] Various methods for removing carbon dioxide from the air are known: as is described in DE 699 02 409, the air can be passed through a zeolite filling that absorbs the carbon dioxide until the filling is saturated. At greater throughputs, the pressure-reversal method is used, as described in DE 696 15 289. Not further referred to, but used as a standard in laboratories, is potash production, in which the potassium hydroxide is converted into potassium carbonate by the absorption of CO₂.

[0013] Exactly why the absorption of CO₂ in the electrodes is not possible under certain operating conditions has not yet been explained. There are, however, a number of observations that confirm that electrodes that have a good wetting capability tend to carbonize, in contrast to which strongly hydrophobic electrodes do not exhibit such behaviour. A sufficiently high degree of hydrophobicity can be achieved by adding large quantities of PTFE powder, as is widely discussed in the literature. However, this also reduces gas exchange, and the performance of the electrode is diminished. In order to produce an electrode that is suitable for operation with air that contains CO₂, all the parameters that constitute hydrophobicity must be fulfilled:

[0014]

- Hydrophobic catalyst surface:

The hydrophobicity of the smallest pores of the gas diffusion electrode is adjusted by the wetting properties of the catalyst. In this connection, silver is distinguished by a maximal 2-molecular wetting. For amalgamated silver surface, the wetting is, in fact, monomolecular.

- Hydrophobic binding agent:

Because of poor wettability, as the binding agent in the electrode, PTFE can hydrophobize the pores in the range from a few tenths of a millimeter to 5 µm.

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Uniform hydrophobizing can be achieved by producing a suspension or by "reactive mixing."

- Hydrophobic pore size:

The macroscopic pore radii that can no longer be flooded with electrolyte under the conditions discussed heretofore ensue from the Hagen-Poiseuille Law and from operating conditions. Depending on gas-pressure ratio, this lies between 5 and 20 μm .

- pH value:

An additional value sets the pH value of the catalyst. The measurement of such pH values is customary for catalysts that contain carbon. Any calcium carbonate that is present will be immediately be broken down again into potassium hydroxide and carbon dioxide by an acid surface.

[0015] In particular, the pore size is difficult to adjust in the case of rolled electrodes because at the rolling pressure that is needed, it is possible that the large pores in the pore system will collapse. For this reason, the present invention relates to an improved method, in which the size of the pores and the remaining parameters can be so adjusted that carbonization no longer takes place during electrolysis operation.

[0016] The following is done in order to prevent this collapsing: analogously to the method described in WO 03/004726 A2, a two-stage process is followed when fabricating the electrode band. The catalyst/PFTE mixture is first rolled out to form a thin band in a first calendar, and this is then introduced into a metal carrier in a second calendar. As described therein, a filler is added to the catalyst powder, and this absorbs the rolling force in the first calendar.

[0017] Unlike the method described in WO 03/004726 A2, this filler is removed ahead of the second calendar by a heating device such as a hot-air blower. In this way, an electrode moves into the second calendar with a defined pore radius. Because of the fact that this second calendar presses the electrode into a metal carrier by applying a small

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amount of pressure, and because it is possible to measure the change in the thickness of the electrode, the reduction in the size of the pore system can also be measured. Thus, the hydrophobic pore size can be adjusted by adjusting the calendar gap.

- 5 [0017a] In a method aspect, the invention relates to a method for producing a gas diffusion electrode from a silver catalyst on a PTFE-substrate, comprising the steps of: (a) filling a pore system of the silver catalyst with a wetting agent; (b) mixing a dimensionally-stable solid body having a particle size that is greater than the particle size of the silver catalyst with the silver catalyst; (c) shaping the thus obtained
10 compression-stable mass into a homogeneous catalyst band in a first calender; and (d) in a second calender, embossing an electrically conducting material into the catalyst band, wherein an interim heating takes place between the first and second calenders by means of a heater, such that at least a part of the wetting agent is removed.
- 15 [0017b] In a product aspect, the invention relates to a gas diffusion electrode fabricated by the method defined above.

[0018] Long-term tests have shown that even in the presence of atmospheric CO₂, carbonization no longer occurs with GDE electrodes fabricated in this way, and that continuous operation is possible.

- 20 [0019] The method used to fabricate the GDE is shown in greater detail in Figure 1.

- [0019a] The following reference numbers 1 to 16 and the associated description corresponding to those in WO 03/004726 A2. The electrode skin 8 that emerges from the skin calendar 7, the first calendar, is routed into the
25 heating device 17, where the electrode skin is so heated that the filler is driven out of the electrode skin. The heating can be effected by both radiation and by the application of hot air. Combinations of both methods are also possible.

[0020]

Reference numbers

- 1 Rotary slide
- 2 Supply hopper
- 3 Beater mill
- 4 Powder funnel
- 5 Beater
- 6 Light barrier
- 7 Skin calendar
- 8 Electrode skin
- 9 Guide rail
- 10 Wetting roller
- 11 Wetting roller
- 12 Deflection roller
- 13 Stripper system
- 14 Edge stripper
- 15 Spool for electrode band
- 16 Drive motor
- 17 Heating system

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CLAIMS:

1. A method for producing a gas diffusion electrode from a silver catalyst on a PTFE-substrate, comprising the steps of:

(a) filling a pore system of the silver catalyst with a wetting agent;

5 (b) mixing a dimensionally-stable solid body having a particle size that is greater than the particle size of the silver catalyst with the silver catalyst;

(c) shaping the thus obtained compression-stable mass into a homogeneous catalyst band in a first calender; and

10 (d) in a second calender, embossing an electrically conducting material into the catalyst band,

wherein an interim heating takes place between the first and second calenders by means of a heater, such that at least a part of the wetting agent is removed.

2. A gas diffusion electrode fabricated by the method of claim 1.

Fig. 1