



(72) STARBECK, Gerhard (Deceased), DE

(72) WAIDHAS, Manfred, DE

(72) GRÜNE, Horst, DE

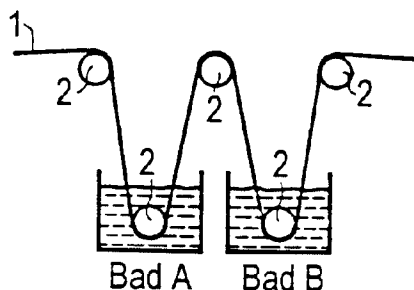
(72) BIRKLE, Siegfried, DE

(71) SIEMENS AKTIENGESELLSCHAFT, DE

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(54) **PROCEDE DE PRODUCTION D'UNITES A MEMBRANE ET
ELECTRODES POUR PILES A COMBUSTIBLE A
MEMBRANE D'ELECTROLYTE POLYMERE**
(54) **METHOD OF PRODUCING MEMBRANE ELECTRODE UNITS
FOR PEM FUEL CELLS**



(57) L'invention concerne un procédé selon lequel des unités à membrane et électrodes pour piles à combustible sont produites en continu et de façon pouvant être automatisée. Une bande constituée d'une membrane polymère est tout d'abord tirée à travers un bain contenant une solution saline du matériau d'électrode, de sorte que la bande est recouverte, sur ces deux côtés, d'une croûte ou d'un film de sel, puis le sel adhérent à ladite bande est réduit dans un courant de gaz ou dans un autre bain.

(57) The invention concerns a method wherein membrane electrode units for fuel cells are produced in a continuous and automatable process. A web of polymer membrane is initially drawn through a bath containing a salt solution of the electrode material so that the web has a salt crust or film on both sides, and the salt adhering is then reduced in a stream of gas or in another bath.

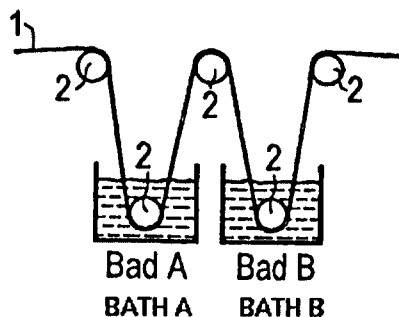


PCT
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<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top; padding: 5px;"> (21) Internationales Aktenzeichen: PCT/DE97/01322 (22) Internationales Anmeldedatum: 25. Juni 1997 (25.06.97) (30) Prioritätsdaten: 196 25 614.3 26. Juni 1996 (26.06.96) DE (71) Anmelder (für alle Bestimmungsstaaten ausser US): SIEMENS AKTIENGESELLSCHAFT [DE/DE]; Wittelsbacherplatz 2, D-80333 München (DE). (71) Anmelder (nur für US): STARBECK, Elsbeth (Erbin des verstorbenen Erfinders) [DE/DE]; Effeltricher Strasse 32, D-90411 Nürnberg (DE). (72) Erfinder: STARBECK, Gerhard (verstorben). (72) Erfinder; und (75) Erfinder/Anmelder (nur für US): WAIDHAS, Manfred [DE/DE]; Schnieglinger Strasse 285, D-90427 Nürnberg (DE). GRÜNE, Horst [DE/DE]; Altenseestrasse 6, D-91341 Röttenbach (DE). BIRKLE, Siegfried [DE/DE]; Veit-Stoss-Strasse 46, D-91315 Höchstadt (DE). </td> <td style="width: 50%; vertical-align: top; padding: 5px;"> (81) Bestimmungsstaaten: CA, JP, NO, US, europäisches Patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Veröffentlicht <i>Mit internationalem Recherchenbericht. Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist. Veröffentlichung wird wiederholt falls Änderungen eintreffen.</i> </td> </tr> </table>			(21) Internationales Aktenzeichen: PCT/DE97/01322 (22) Internationales Anmeldedatum: 25. Juni 1997 (25.06.97) (30) Prioritätsdaten: 196 25 614.3 26. Juni 1996 (26.06.96) DE (71) Anmelder (für alle Bestimmungsstaaten ausser US): SIEMENS AKTIENGESELLSCHAFT [DE/DE]; Wittelsbacherplatz 2, D-80333 München (DE). (71) Anmelder (nur für US): STARBECK, Elsbeth (Erbin des verstorbenen Erfinders) [DE/DE]; Effeltricher Strasse 32, D-90411 Nürnberg (DE). (72) Erfinder: STARBECK, Gerhard (verstorben). (72) Erfinder; und (75) Erfinder/Anmelder (nur für US): WAIDHAS, Manfred [DE/DE]; Schnieglinger Strasse 285, D-90427 Nürnberg (DE). GRÜNE, Horst [DE/DE]; Altenseestrasse 6, D-91341 Röttenbach (DE). BIRKLE, Siegfried [DE/DE]; Veit-Stoss-Strasse 46, D-91315 Höchstadt (DE).	(81) Bestimmungsstaaten: CA, JP, NO, US, europäisches Patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Veröffentlicht <i>Mit internationalem Recherchenbericht. Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist. Veröffentlichung wird wiederholt falls Änderungen eintreffen.</i>
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(54) Title: METHOD OF PRODUCING MEMBRANE ELECTRODE UNITS FOR PEM FUEL CELLS

(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG VON MEMBRAN-ELEKTRODENEINHEITEN (ME) FÜR POLYMER-ELEKTROLYT-MEMBRAN (PEM)-BRENNSTOFFZELLEN



(57) Abstract

The invention concerns a method wherein membrane electrode units for fuel cells are produced in a continuous and automatable process. A web of polymer membrane is initially drawn through a bath containing a salt solution of the electrode material so that the web has a salt crust or film on both sides, and the salt adhering is then reduced in a stream of gas or in another bath.

(57) Zusammenfassung

Die Erfindung betrifft ein Verfahren, bei dem in einem kontinuierlichen und automatisierbaren Prozess Membran-Elektrodeneinheiten für Brennstoffzellen hergestellt werden. Dabei wird ein Band aus polymerer Membran zunächst durch ein Bad mit einer Salzlösung des Elektrodenmaterials so gezogen, daß es beidseitig eine Salzkruste oder einen Salzfilm aufweist, und dann wird das anhaftende Salz im Gasstrom oder in einem weiteren Bad reduziert.

FILE, PRINTING AREA

METHOD FOR MANUFACTURING MEMBRANE ELECTRODE UNITS (ME) FOR POLYMER-ELECTROLYTE MEMBRANE (PEM) FUEL CELLS

The invention is directed to a continuous and automatable method for
5 manufacturing ME (membrane electrode) units for PEM fuel cells that is cost-
beneficial and suitable for mass production.

In previously known methods for manufacturing electrodes for fuel
cells (FC), the desired electrode material is produced in a first method step, this
electrode material being applied onto the electrolyte or onto a carrier such as,
10 for example, carbon paper in a further method step. The application can ensue
by mechanical "doctoring" or by applying a suspension (ink or paste) onto the
membrane and subsequent evaporation of the solvent.

In addition to this method, wherein the electrode material must be
manufactured and insulated in a first stage before it can be applied onto the
15 electrolyte (polymer membrane) in a second method stage, there are also
methods wherein the electrode material is produced directly on the electrolyte.

Included therein is a method wherein the electrode material, for
example platinum, is deposited on the electrolyte from the vapor phase. What
is disadvantageous about this method is that it is also poorly suited for a
20 continuous manufacture -- due to the required evacuation process -- because a
membrane web cannot be drawn through a vacuum without having the
vacuum collapse. Moreover, porous catalyst layers are difficult to realize given
this method.

Another method is known wherein the electrode material is produced
25 in situ on the membrane. H. Takenaka and E. Torikai et al. disclose this in
Int. J. Hydrogen Energy 7, 397 (1982). The membrane is thereby stretched
between two half-cells, so that it separates the two electrolyte spaces of the
half-cells from one another. A salt solution of the desired electrode material

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(for example, thus, an H_2PtCl_6 solution) is placed at the one side of the membrane; a suitable reduction agent is placed at the other side. The reduction agent diffuses to the side of the Pt-containing solution. The encounter of the reduction agent with the $PtCl_6^{2-}$ ions thereby leads to a precipitation of a platinum layer in the surface region of the membrane. This method is fixed in time by the given diffusion rates of the reactants. Over and above this, this method must be applied twice in order to produce a complete (ME) since only one side of the membrane can be coated in one method step.

In view of the future significance of all fuel cells and, in particular, of the PEM fuel cells as energy converters of the future, there is thus a need to offer an improved method for the automated and cost-beneficial manufacture of the core of every PEM fuel cell, namely the ME. It is therefore an object of the present invention to make a method available with which ME for PEM fuel cells can be manufactured in a continuous and automatable process.

The general perception of the invention is that an adequately thick salt crust or a salt film (dependent on the amount of remaining solvent) adheres to the membrane web as a result of simply dipping the electrolyte membrane web into a salt solution of the electrode material, and that, after reduction has ensued, the electrode material adheres to the polymer in the desired penetration depth and mass.

The subject matter of the present invention is a method for the continuous manufacturings [sic] of membrane electrode units for polymer-electrolyte membrane (PEM) fuel cells, whereby a polymer-electrolyte membrane passing through web-shaped

- is drawn such through a solution of a salt of the electrode material in a first method step that the salt adheres to both sides of the membrane in an amount adequate for forming the electrodes, and, then,
- the salt on the membrane is reduced to the electrode material in solution or in the gas stream in a second method step.

In an advantageous development of the invention, a drying step for removing the solvent that adheres to the membrane web is also interposed between the two method steps.

5 In preferred embodiment, the second method step, i.e. the reduction of the adhering salts, is implemented in the gas stream and, potentially, under temperature elevation.

However, the embodiment is advantageous wherein the membrane web is simply conducted over deflection rollers through two baths, first through one that contains the salt and subsequently through one that contains the
10 reduction agent.

What are referred to as "membrane webs" or "electrolyte webs" or "polymer membrane webs" are all processable webs of polymers that conduct protons (or conduct hydroxide ions as well) that can be employed as electrolytes of PEM fuel cells. Let sulfonated polystyrol webs or Nafion
15 (registered trademark), which is a perfluorinated polymer, be cited here by way of example.

Both the smooth, proton-conducting electrolyte membrane as well as a membrane partially provided with carrier material or current collectors such as, for example, carbon paper or fabric can be employed in the inventive
20 method. Given the latter, the immersion time of the membrane changes tremendously because the carrier material is very rapidly saturated with the salt solution.

What are referred to as "electrode material" or "electro-catalyst" are the electrodes standard for PEMFC, particularly precious metals such as, for
25 example, platinum or ruthenium. Alloy electrodes can be manufactured from correspondingly mixed salt solutions.

What are referred to as "solution of a salt of electrode material" are salt solutions of the aforementioned substances and compounds, i.e., for example, the solution of a platinum salt with Pt^{4+} ions such as a 2-molar solution of

hexachloroplatinate in water. Of course, Pt^{2+} or arbitrary mixtures of metal salts such as, for example, a mixture of Pt^{2+} salts with Ru^{3+} salts for producing Pt/Ru catalysts for the direct-methanol fuel cell can be present. Neither the salt cited here by way of example nor said metal or solvent are intended to
5 limit the scope of the invention.

The salt concentration prevailing in the solution is, of course, dependent on the desired thickness or penetration depth of the salt crust as well as on the area that the electrode should occupy on the electrolyte web. The occupation of the membrane with salt can be controlled by the
10 concentration of the salt solution.

In general, the web is pulled through the salt solution with a speed > 0 ; however, it is also possible that the web dwells in the salt solution, i.e. that the continuous and automated process repeatedly provides holding times. The penetration depth of the electrode material in the membrane (depth
15 distribution of the electro-catalyst in the polymer electrolyte can be controlled via the dwell time of the membrane in the salt bath.

The properties of the manufactured ME can be varied in a broad range by the suitable selection of the reaction conditions (salt, reduction agent, solvent, thixotropy, viscosity, pH value, concentrations, bath and ambient
20 temperature) and by addition of additives (for example, binders). This variation is also possible by subsequent after-treatment of the occupied electrolyte polymer web such as adding current collectors (for example, carbon fabric), pressing, impregnation, tempering or the like.

All standard reduction agents that leave the membrane material and the
25 manufactured ME undamaged (specifically in view of poisonings), that can be removed residue-free and thereby quantitatively reduce the adhering salt under optimally mild conditions are suitable for the reduction of the salt adhering to the membrane. Examples are, for instance, hydrogen or diamide.

The invention is described in greater detail below on the basis of the two Figures. The aforementioned definitions are valid not only for the specification and claims but also for the terms employed in the explanation of the Figures.

5 Figure 1 shows the preferred embodiment of the method wherein the occupation of the membrane web with salt ensues in a bath A and the reduction of the adhering salt ensues in a further bath B.

10 Figure 2 shows another preferred embodiment of the invention wherein the membrane web is first occupied with salt in a bath A and the adhering salt is then reduced in the gas stream.

15 First, the polymer-electrolyte membrane web 1 passing through web-like can be seen in Figure 1. Via a first deflection roller 2, the membrane web proceeds into the bath A in which the salt or the salt mixture is found in an inert solvent, preferably water or some other solvent with a high dielectric constant. Upon passage through the bath A, the membrane is occupied with the salt from the solution on both sides, and a salt film or a salt crust is on both sides of the web 1 when the web 1 emerges from the bath A. The web 1 covered with salt is conducted over the next deflection roller 2 into the bath B in which the reduction agent is situated, likewise in an inert solvent. The salt adhering to the web 1 is thereby reduced when passing through the bath B. 20 Via the last deflection roller 2 at the extreme right end of Figure 1, the web 1 proceeds as finished ME into further processing such as, for example, into a cutting machine. Later, the electrode structure can be optimized with a press, potentially with following thermal treatment.

25 Figure 2 likewise shows a web of polymer-electrolyte membrane 1 passing through web-like that is steered via deflection rollers 2 into, first, the bath A that, as in Figure 1, contains the salt of the electrode material in

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solution. Upon passage through the bath A, a salt crust forms on the membrane web, and, after leaving the bath A, the encrusted membrane web is pulled through a vessel 3 with reducing atmosphere that potentially has a heating device available to it. Gaseous reduction agent can flow into the vessel
5 3 with reducing atmosphere via the admission opening 4. When it emerges from the vessel 3, both sides of the membrane web are again coated with electrode material.

In the embodiment wherein the reduction of the salt crust on the membrane web ensues in the gas stream, it is advantageous that the mixing of
10 the contents of both baths is avoided in bath B. In the embodiment according to Figure 1, however, this can also be achieved in that a drying mechanism such as, for example, a ventilator or fan that [...] at the level of the deflection roller 2 that dries the web from both sides and rids the salt crust of solvent is interposed between the emergence from the bath A and the entry of the
15 membrane web into the bath B.

The inventive method is distinguished in that both sides of the membrane can be simultaneously covered with an electrochemically active electrode layer in a continuous process and, thus, an ME arises in a single process step. High manufacturing speeds given low costs can thus be achieved
20 by the elimination of discontinuous work steps as well as time-defining, diffusion-limited steps.

Patent Claims

1. Method for the continuous manufacture of membrane electrode units (ME) for polymer-electrolyte membrane (PEM) fuel cells, whereby a polymer-electrolyte membrane (membrane web) passing through web-shaped

- 5 -- is drawn such through a solution of a salt of the electrode material in a first method step that the salt adheres to both sides of the membrane in an amount adequate for forming the electrodes, and, then,
-- the salt on the membrane is reduced in a second method step.

2. Method according to claim 1, whereby the membrane web is pulled
10 through a bath with a solution of the reduction agent or with the fluid reduction agent in the second method step.

3. Method according to claim 1, whereby the membrane web is pulled through a vessel with reducing atmosphere in the second method step.

4. Method according to one of the preceding claims, whereby a drying
15 step for the removal of the solvent on the membrane web is interposed between the two method steps.

5. Method according to one of the preceding claims 1, 3 or 4, whereby the reduction of the salt adhering to the web occurs in the gas stream and upon temperature elevation.

Fetherstonhaugh & Co.
Ottawa, Canada
Patent Agents

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FIG 1

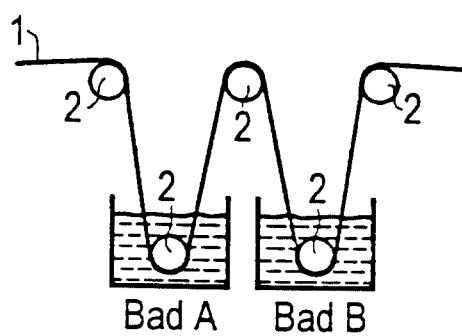


FIG 2

