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(54) Title: IMPROVED STRUCTURES AND PREPARATION METHODS FOR CATALYST COATED MEMBRANES FOR FUEL CELLS

(57) Abrégé/Abstract:

A novel method is disclosed for preparing reinforced catalyst layers for catalyst coated membranes in fuel cells. A hydrophilic expanded polymer sheet (e.g. ePTFE) is used for reinforcement in order to improve the mechanical durability of the catalyst layers. Advantageously, a pure aqueous based catalyst ink can be used in the coating process for preparing the catalyst layers.

Docket No.: P831123/CA/1

ABSTRACT

A novel method is disclosed for preparing reinforced catalyst layers for catalyst coated membranes in fuel cells. A hydrophilic expanded polymer sheet (e.g. ePTFE) is used for reinforcement in order to improve the mechanical durability of the catalyst layers. Advantageously, a pure aqueous based catalyst ink can be used in the coating process for preparing the catalyst layers.

Docket No.: P831123/CA/1

IMPROVED STRUCTURES AND PREPARATION METHODS FOR CATALYST COATED MEMBRANES FOR FUEL CELLS

BACKGROUND

Field of the Invention

This invention relates to simplified methods for fabricating a catalyst coated membrane (CCM) for solid polymer electrolyte membrane fuel cells. The invention further relates to CCM structures comprising reinforcement layers of expanded polymer sheets and which exhibit improved mechanical strength. The improved CCM structures can be fabricated using the simplified methods of the invention.

Description of the related art

Reinforcement is one of the important approaches for improving the durability of a polymer electrolyte membrane fuel cell (PEMFC). For instance, a state-of-art proton exchange membrane (PEM) can be mechanically reinforced by either a porous substrate or nanofibers to improve its mechanical strength and durability. Among the possible reinforcement materials, expanded polytetrafluoroethylene sheet (ePTFE) is probably the one mostly used due to its excellent chemical inertness and stability. Much academic and patent literature has been published in which ePTFE is utilized to improve the mechanical strength and subsequent durability of a PEM during fuel cell operation [e.g. WO2003095552, US8431285, US20030211264, US20130022894, US20140080031, *Journal of Power Sources* 175(2008) 817-825, *Journal of Membrane Science* 306 (2007) 298-306].

In contrast to the PEM, there is little effort being devoted to reinforcing the catalyst layers (i.e. cathode and anode layers) in such fuel cells. It is known that microcracks can form or develop in catalyst layers during catalyst layer fabrication or fuel cell operation (e.g. during freeze-thaw and wet-dry cycles). The microcracks can further generate stress (both chemical and mechanical) to the underlying PEM, which will likely lead to the premature failure of the PEM. Thus, there is a need to develop reinforced catalyst layers for PEMFCs in order to meet long-term durability requirements for automotive applications.

Recently, several patent applications were filed in which porous ePTFE was applied to reinforce the catalyst layers to prevent the formation of cracks and improve the mechanical strength of the catalyst layers (e.g. US20110236788A1; US20120183877A1; US20120189942A1; US20140261981A1; US20140261983A1).

The mechanical stability of the catalyst layer was improved without impacting the performance. However, the hydrophobic nature of ePTFE required the usage of organic solvents in preparing the catalyst ink in order to properly rinse and impregnate the ink into the ePTFE. The presence of organic solvents complicates the CCM coating process, increases safety concerns, and adds extra cost to the process. To avoid the usage of organic solvents, pure aqueous ink would be preferred. Unfortunately, a pure aqueous ink is not compatible with traditional ePTFE and thus reinforcement in this manner has not been reported to date.

The current invention involves a novel method to fabricate a catalyst layer reinforced by an expanded polymer sheet (e.g. ePTFE). In particular, the ePTFE used is hydrophilic which can be achieved by surface treatment. The hydrophilicity of the ePTFE allows for the use of aqueous catalyst ink, which simplifies the coating process and reduces the cost. The reinforced catalyst layers show improved mechanical strength compared to their non-reinforced counterparts.

SUMMARY

Here, a novel method is disclosed for preparing reinforced catalyst layers for catalyst coated membranes in fuel cells. A hydrophilic expanded polymer sheet (e.g. ePTFE) is used for reinforcement in order to improve the mechanical durability of the catalyst layers. Advantageously, a pure aqueous based catalyst ink can be used in the coating process for preparing the catalyst layers. The hydrophilic expanded polymer sheet can be prepared by surface treatment of a conventional hydrophobic equivalent. A catalyst coated membrane (CCM) of the invention, containing such reinforced catalyst layers, shows improved mechanical strength compared to conventional unreinforced CCMs (e.g. as indicated by the better electrical resistance characteristics in the following Examples). In addition, the hydrophilicity of the hydrophilic expanded polymer sheets used can help maintain the hydration of the catalyst layers under hot and dry fuel cell operating conditions, which ultimately will improve fuel cell performance.

Specifically, the inventive method is for preparing a catalyst coated membrane assembly for a solid polymer electrolyte fuel cell in which the catalyst coated membrane assembly comprises a solid polymer electrolyte membrane comprising a proton-conducting ionomer and first and second catalyst layers comprising first and second catalysts respectively. The first and second catalyst layers are bonded to first and second sides respectively of the solid polymer electrolyte membrane. And at least the first catalyst layer comprises a hydrophilic expanded polymer sheet. The method comprises the steps of obtaining the hydrophilic expanded polymer sheet, applying the hydrophilic expanded polymer sheet to a polymer backing sheet, preparing a first catalyst ink slurry comprising the first catalyst and an aqueous solvent, coating the first catalyst ink slurry onto the hydrophilic expanded polymer sheet, drying the first catalyst ink coating thereby creating a first catalyst layer comprising the hydrophilic expanded polymer sheet mounted on the backing sheet, and decal transferring the first catalyst layer to the first side of the solid polymer electrolyte.

In one embodiment, the first catalyst layer can be the cathode catalyst layer and the first catalyst can be the cathode catalyst. Alternatively, the first catalyst layer can be the anode catalyst layer and the first catalyst can be the anode catalyst. In a preferred embodiment, both the first and second catalyst layers comprise a hydrophilic expanded polymer sheet.

In the CCMs of the invention, the proton-conducting ionomer can be perfluorosulfonic acid ionomer or hydrocarbon ionomer. The expanded polymer sheet can be an expanded PTFE (ePTFE) sheet. The polymer backing sheet can be polyethylene terephthalate. The first catalyst ink slurry can additionally comprise other common constituents used in the art, e.g. Pt/carbon or Pt alloy/carbon and perfluorosulfonic acid ionomer.

The decal transferring step can comprise the steps of applying the first catalyst layer comprising the hydrophilic expanded polymer sheet mounted on the backing sheet against the first side of the solid polymer electrolyte membrane, hot pressing the applied first catalyst layer and the solid polymer electrolyte membrane together at 150 °C at an applied force of 5000 lb for 3 minutes, then removing the backing sheet.

The invention further comprises a catalyst coated membrane assembly for a solid polymer electrolyte fuel cell made according to the aforementioned methods and a solid polymer electrolyte fuel cell comprising a catalyst coated membrane assembly made according to the aforementioned methods.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 schematically illustrates processes of the invention for catalyst coating and for fabrication of a half CCM.

Figure 2 shows various SEM images of hydrophilic ePTFE, catalyst layers, and a half CCM which have been reinforced in accordance with the invention. Figure 2A shows the morphology of hydrophilic porous ePTFE; Figure 2B shows a cross-sectional image of a catalyst layer reinforced by hydrophilic ePTFE; Figure 2C shows a cross-sectional image of a reinforced catalyst layer with catalyst missing; and Figure 2D shows a cross-sectional image of a half CCM comprising a reinforced catalyst layer on Nafion membrane (EW= 875).

Figure 3A shows a photograph of a reinforced catalyst layer being peeled from a PET backing substrate. Figure 3B shows a photograph of the handling of a free-standing catalyst layer reinforced by hydrophilic ePTFE.

Figure 4 shows a schematic illustration of the apparatus used in the breakdown voltage testing performed in the Examples.

DETAILED DESCRIPTION

Herein, a material (and particularly an expanded polymer sheet) is considered to be "hydrophilic" if it exhibits a static water contact angle of less than 30°.

In the present invention, a hydrophilic expanded polymer sheet (such as ePTFE) is employed as a coating substrate onto which is cast an aqueous ink. The aqueous ink coats, wets, and fills the porous expanded polymer sheet. Moreover, this ePTFE will further serve as a reinforcement layer to improve the mechanical strength of the catalyst layer, consequently improving the durability of a CCM and a MEA made therewith. In addition, the hydrophilicity of the ePTFE used can help maintain the hydration of the catalyst layer under hot and dry fuel cell operation conditions, which will ultimately improve the fuel cell performance.

Figure 1 schematically illustrates processes of the invention for catalyst coating and for fabrication of a half CCM. A layer of hydrophilic ePTFE is initially obtained, for instance via wet chemical treatment or surface plasma polymerization of conventional hydrophobic ePTFE (e.g. CA2864541). As shown in Figure 1, the hydrophilic ePTFE layer is first laid onto a polyethylene terephthalate (PET) substrate under controlled tension. Subsequently, a desired aqueous catalyst ink (e.g. containing Pt/carbon catalyst, Aquivion (EW=790) ionomer, and water as solvent) can be cast onto the ePTFE via Mayer bar coating. The ink is readily impregnated into the ePTFE and will form a thin wet layer between the ePTFE and the underlying PET substrate. A thin layer of partially impregnated ePTFE layer thus forms adjacent to the PET. The viscosity of the ink, thickness, porosity, and pore size of ePTFE can have significant impact on the properties and morphology of the formed catalyst layer. A lower ink viscosity combined with thinner ePTFE with larger pore size and higher porosity can result in more thorough impregnation and uniform reinforcement. After evaporation of the water solvent, the catalyst layer can be transferred onto a PEM (e.g. Nafion type membrane) via hot bonding (decal transfer). Due to the very low adhesion force between the PET and the ePTFE, such decal transfer can be smooth and complete.

The following Examples have been included to illustrate certain aspects of the invention but should not be construed as limiting in any way.

EXAMPLES

Hydrophilic ePTFE samples, reinforced catalyst layers, and half CCMs were prepared as described below.

Surface plasma polymerization to prepare hydrophilic ePTFE

Hydrophilic ePTFE with a static water contact angle of 10° was prepared from conventional sheets of hydrophobic ePTFE that was pre-treated via surface polymerization of allylamine (as disclosed in the aforementioned CA2864541). Plasma treatment was performed on a M4L plasma system provided by PVA Tepla Co. Ltd. The ePTFE was pre-cut into 15 cm × 15 cm size and placed on the plate of the plasma chamber. The thickness of the ePTFE was about 4 μm, while the porosity and pore size was 90% and 1.2 μm respectively. The chamber was evacuated to 50 mTorr at a speed of 40 L/min. Then, nitrogen gas was injected at a rate of 100 standard cubic centimeters (SCCM) with a glow discharge at 75 W for 3 minutes. The system was evacuated to 100 mTorr. Then, allylamine was injected at a speed of 18 SCCM untill the pressure reached 300 mTorr. Radio frequency (RF) glow discharge power was set at 150 W and the treatment time was 10 min. Thereafter, the system was evacuated again to a pressure below 50 mTorr and air was introduced into the chamber to atmospheric pressure for 15 min. Treated ePTFE film was removed from the chamber and stored between two pieces of examining paper before further usage.

Catalyst ink slurry preparation

0.5 g of Pt catalyst deposited on carbon particles plus 50 g of grinding media (5 mm Yttria-stablized zirconia beads) were mixed with 5g of distilled and deionized water and 2g of perfluorosulfonic acid polymer dispersion (Aquivion 790). The ink slurry was jar milled for several days before usage.

Preparation of reinforced catalyst layers

The ePTFE (10 cm ×10 cm) treated by surface polymerization of allylamine was laid carefully on a polyethylene terephthalate (PET) substrate. Wrinkles and air bubbles were minimized to avoid coating defects. The catalyst ink slurry prepared as above was coated onto the ePTFE with a loading of 0.25 mg/cm^2. The coating substrate was then dried on a hot plate at 55°C for 30 minutes before usage.

Preparation of half CCMs

Membrane electrolyte was fabricated by coating a layer of Nafion 875 ionomer solution (20% solids content, n-propanol/water = 60/40) onto a casted PTFE (polyethylene tetrafluoroethylene polymer) substrate (from Saint-Gobain) via knife coating. After quick drying, the coating substrate was annealed at 150 °C for 30 minutes to produce a membrane electrolyte layer on the PTFE substrate. The thickness of the membrane electrolyte layer was about 15 μm. The reinforced catalyst layer prepared as above was then decal transferred to the Nafion 875 membrane via hot bonding at 150 °C with applied force of 5000 lb for 3 minutes.

The SEM image in Figure 2A shows the morphology of the prepared hydrophilic porous ePTFE. In Figure 2A, a porous structure was observed for the hydrophilic ePTFE. Figure 2B shows a cross-sectional SEM image of a catalyst layer reinforced by hydrophilic ePTFE on a PET substrate. Beneath a uniform catalyst coating, a very thin interface containing ePTFE was observed. By cracking the catalyst layer, the internal structure of the reinforcement layer was better observed (as shown in the SEM image of Figure 2C which shows a cross-sectional image of the reinforced catalyst layer with catalyst missing). A continuous porous ePTFE layer was present, which supported the catalyst layer. It is noted that the adhesion force between the ePTFE and the PET backer was sufficient to keep the ePTFE from contracting during the drying process. After decal transfer of the catalyst layer to a Nafion 875 membrane, a half CCM was obtained. (Figure 2D shows a cross-sectional image of the half CCM which comprises the reinforced catalyst layer on Nafion membrane, EW= 875.) It is noted in particular that, on the top of the catalyst layer, a very thin layer of ePTFE was observed, which can function as a protection layer to prevent catalyst cracking during fuel cell operation, as well as to prevent penetration of carbon fibres from the adjacent gas diffusion layer. Due to the high porosity and large pore size, this thin layer of ePTFE did not cause a significant increase of electrical resistance in the catalyst layer under compression. Moreover, the hydrophilicity of the ePTFE is helpful for maintaining the hydration level of the catalyst layer during fuel cell operation, which should therefore improve the fuel cell performance, particularly under hot and dry operating conditions.

Figure 3A shows a photograph of a reinforced catalyst layer being peeled off from the PET backing substrate. As is evident from the photograph, the reinforced catalyst layer can be readily peeled off. Figure 3B shows a photograph of the handling of the peeled off, free-standing catalyst layer of Figure 3A. As is evident from the photograph, the peeled off catalyst layer can be easily handled without compromising the original shape. These examples demonstrate the improved mechanical strength of the reinforced catalyst layer. To the best of our knowledge, this is the first report of free-standing catalyst layer being fabricated.

To study the effect of reinforcement layer on the potential for electrical shorting through the catalyst layer, a series of breakdown voltage (BDV) tests were carried out. Figure 4 shows a schematic illustration of the apparatus used in this BDV testing. As illustrated in Figure 4, a BDV testing setup including a pair of carbon plates, copper based compression heads, and power supply was used to test the breakdown voltage of half CCMs.

Sample preparation for breakdown voltage testing

First, a pair of carbon plates was pre-cut into 4 cm × 4 cm, followed by surface polishing using extra fine sandpaper (e.g. Buehler P2500). A piece of reinforced half CCM prepared as above was cut into 5 cm × 5 cm size and assembled between two Toray GDL samples (3 cm × 3 cm) so as to create a GDL/half CCM/GDL sandwich assembly. The sandwich assembly was then hot bonded at 150 °C with applied force of 5000 lb for 1.5 minutes. After bonding, the test sample was placed on the top of bottom carbon plate, followed by aligning the top carbon plate. Then the whole assembly was moved to the bottom plate of the BDV head. On the top of the assembly, one piece of Grafoil® sheet was added to uniformly distribute the compression. The Grafoil® sheet was hot compressed prior to usage at 150 °C, 7000 lbs for 5 minutes.

Breakdown voltage testing of prepared samples involved applying an increasing voltage across the sample until voltage breakdown occurred.

Four different samples with reinforced catalyst layers and four different samples without reinforced catalyst layers were prepared, tested, and compared. The breakdown voltages observed for the catalyst layers without reinforcement were 1.6, 1.8, 1.6, and 1.6 volts respectively. The breakdown voltages observed for the catalyst layers with reinforcement were much higher, namely 35, 37, 50, and 32 volts respectively. The electrolyte membrane used in the sample fabrication was 15 micron thick, Nafion membrane (D2029, EW=875) which was cast in-house. Due to the rough edges present on the GDLs, the samples without reinforcement showed very low BDVs, i.e. about 1.6 volts on average. In contrast, the samples with the reinforced catalyst layers showed much higher BDV, i.e. >30 volts, verifying the protective effect of the hydrophilic ePTFE reinforcement.

All of the above U.S. patents, U.S. patent application publications, U.S. patent applications, foreign patents, foreign patent applications and non-patent publications referred to in this specification, are incorporated herein by reference in their entirety.

While particular elements, embodiments and applications of the present invention have been shown and described, it will be understood, of course, that the invention is not limited thereto since modifications may be made by those skilled in the art without departing from the spirit and scope of the present disclosure, particularly in light of the foregoing teachings. Such modifications are to be considered within the purview and scope of the claims appended hereto.

WHAT IS CLAIMED IS:

1. A method of preparing a catalyst coated membrane assembly for a solid polymer electrolyte fuel cell, the catalyst coated membrane assembly comprising a solid polymer electrolyte membrane comprising a proton-conducting ionomer, first and second catalyst layers comprising first and second catalysts respectively and bonded to first and second sides respectively of the solid polymer electrolyte membrane, wherein the first catalyst layer comprises a hydrophilic expanded polymer sheet; the method comprising:

obtaining the hydrophilic expanded polymer sheet;
applying the hydrophilic expanded polymer sheet to a polymer backing sheet;
preparing a first catalyst ink slurry comprising the first catalyst and an aqueous solvent;
coating the first catalyst ink slurry onto the hydrophilic expanded polymer sheet;
drying the first catalyst ink coating thereby creating a first catalyst layer comprising the hydrophilic expanded polymer sheet mounted on the backing sheet; and
decal transferring the first catalyst layer to the first side of the solid polymer electrolyte.

2. The method of claim 1 wherein the first catalyst layer is the cathode catalyst layer and the first catalyst is the cathode catalyst.

3. The method of claim 1 wherein the first catalyst layer is the anode catalyst layer and the first catalyst is the anode catalyst.

4. The method of claim 1 wherein both the first and second catalyst layers comprise a hydrophilic expanded polymer sheet.

5. The method of claim 1 wherein the proton-conducting ionomer is perfluorosulfonic acid ionomer or hydrocarbon ionomer.

6. The method of claim 1 wherein the expanded polymer sheet is an expanded PTFE sheet.

7. The method of claim 1 wherein the polymer backing sheet is polyethylene terephthalate.

8. The method of claim 1 wherein the first catalyst ink slurry additionally comprises Pt/carbon or Pt alloy/carbon and perfluorosulfonic acid ionomer.

9. The method of claim 1 wherein the decal transferring step comprises:

applying the first catalyst layer comprising the hydrophilic expanded polymer sheet mounted on the backing sheet against the first side of the solid polymer electrolyte membrane;

hot pressing the applied first catalyst layer and the solid polymer electrolyte membrane together at 150 °C at an applied force of 5000 lb for 3 minutes; and

removing the backing sheet.

10. A catalyst coated membrane assembly for a solid polymer electrolyte fuel cell made according to the method of claim 1.

11. A solid polymer electrolyte fuel cell comprising a catalyst coated membrane assembly made according to the method of claim 1.

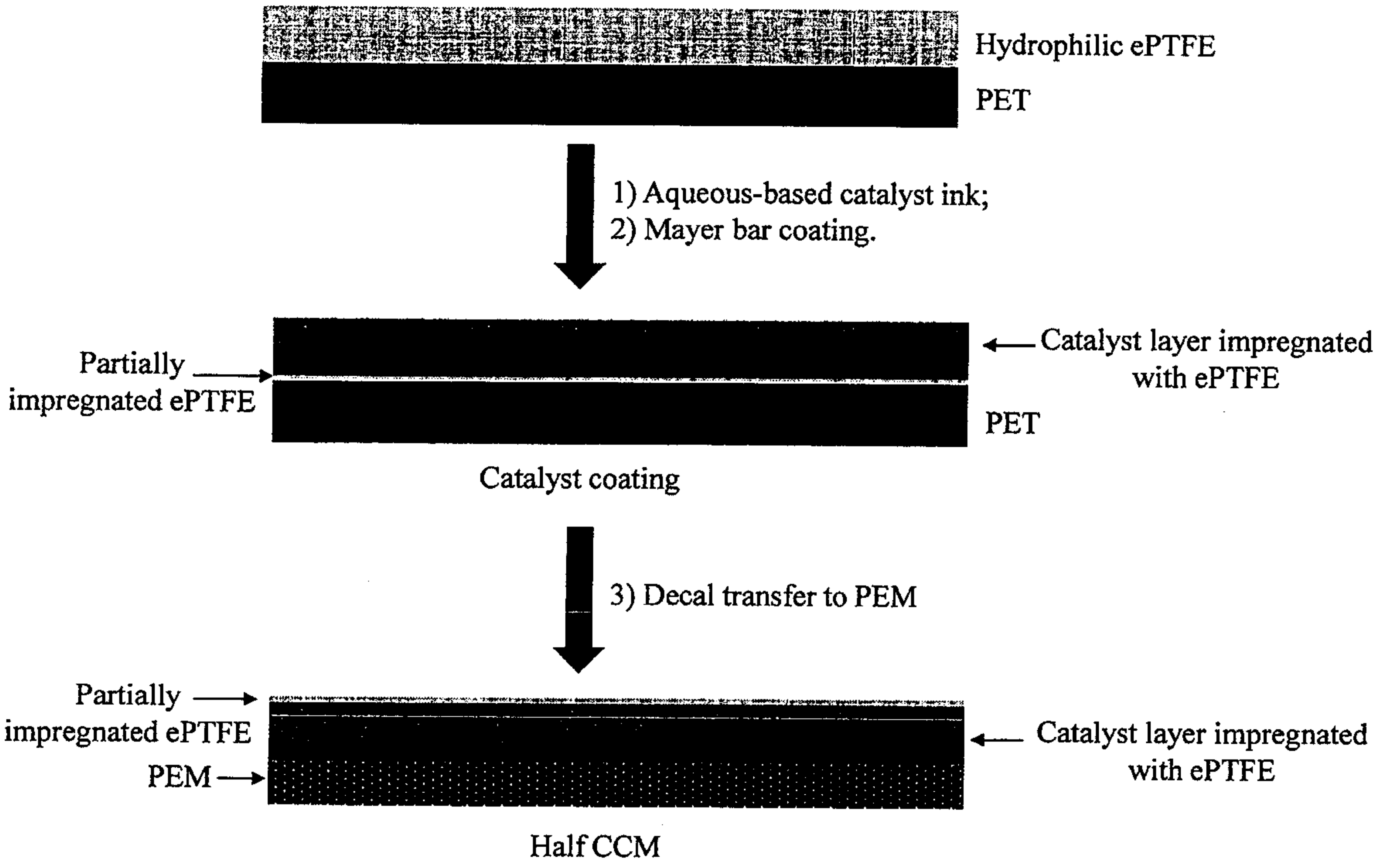
Hydrophilic ePTFE
PET
1) Aqueous-based catalyst ink;
2) Mayer bar coating.
Partially impregnated ePTFE
Catalyst layer impregnated with ePTFE
PET
Catalyst coating
3) Decal transfer to PEM
Partially impregnated ePTFE
PEM
Catalyst layer impregnated with ePTFE
Half CCM

FIG. 1

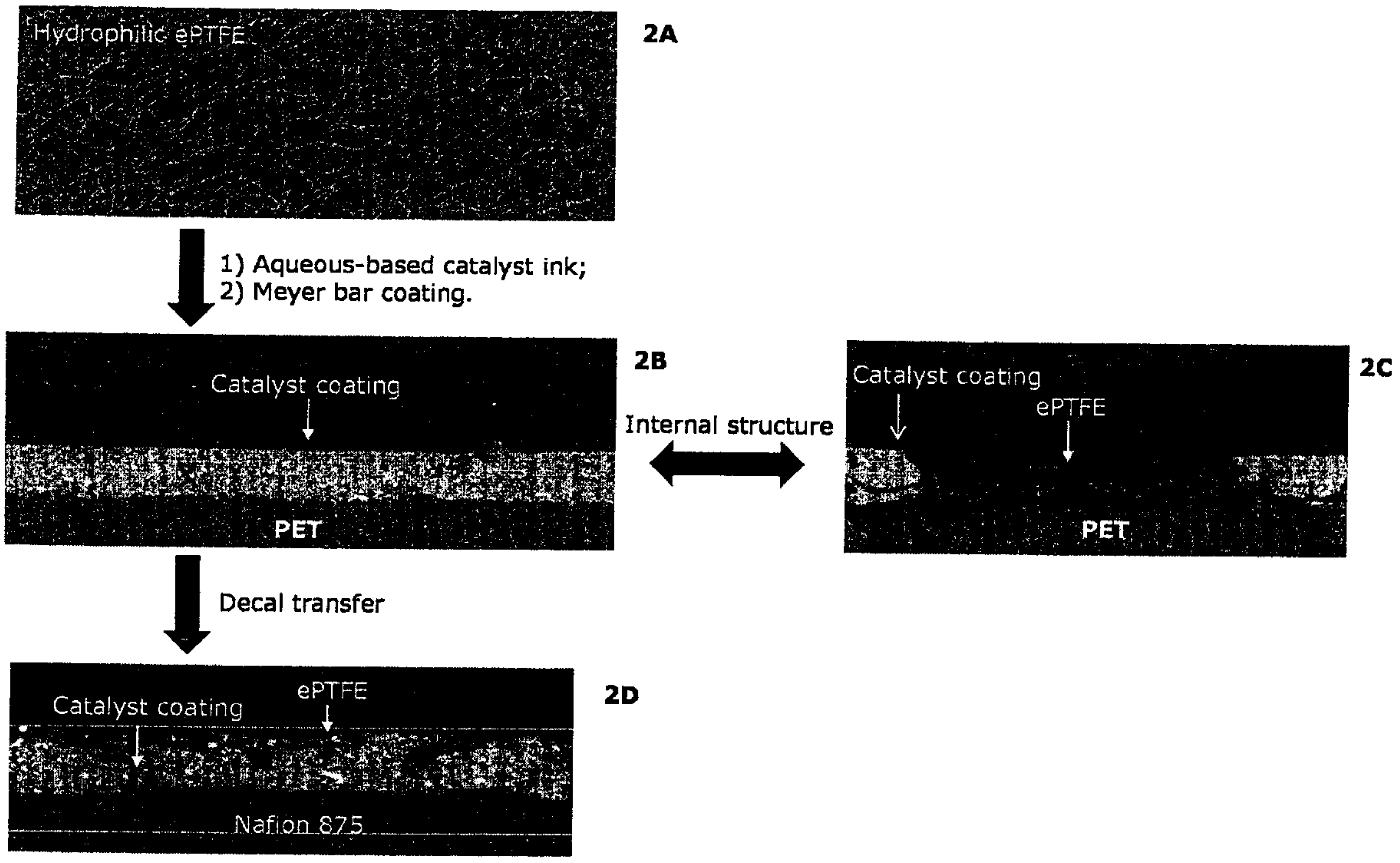
Hydrophilic ePTFE
2A
1) Aqueous-based catalyst ink;
2) Meyer bar coating.
Catalyst coating
2B
PET
Internal structure
Catalyst coating
ePTFE
2C
PET
Decal transfer
Catalyst coating
ePTFE
2D
Nafion 875

FIG. 2

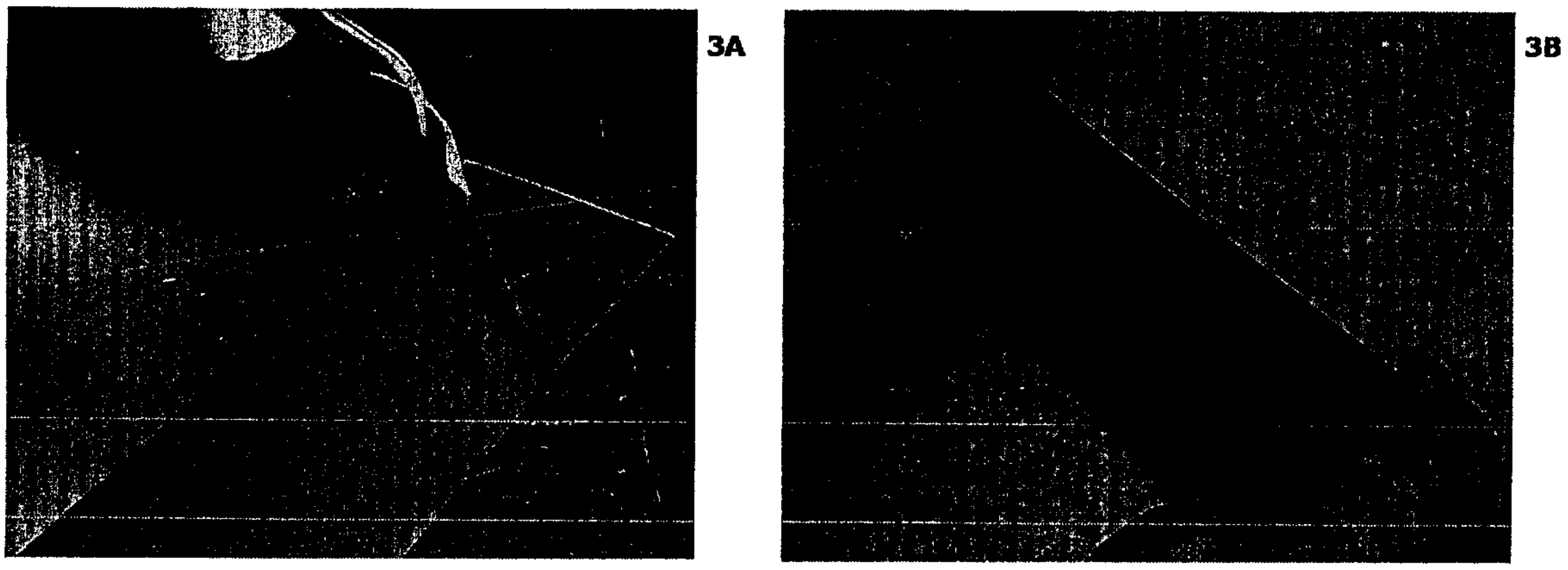

FIG. 3

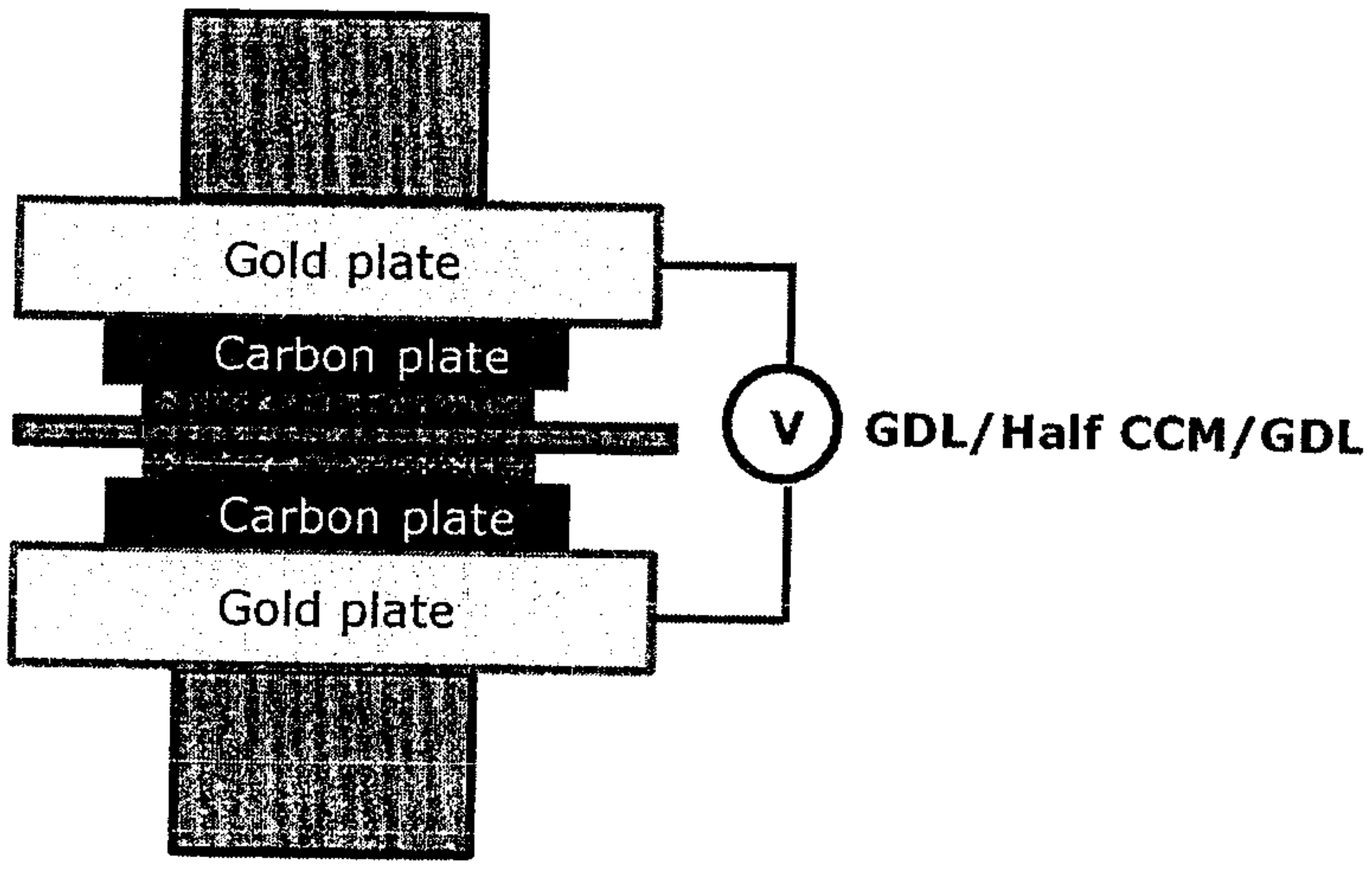
Gold plate
Carbon plate
V
GDL/Half CCM/GDL
Carbon plate
Gold plate

FIG. 4