**MASS MANUFACTURE OF MEAs USING HIGH SPEED DEPOSITION PROCESSES****Grant agreement no.: 779591****Start date: 01.01.2018 – Duration: 36 months****Project Coordinator: Technische Universität Chemnitz****DELIVERABLE REPORT****DELIVERABLE D1.2 - REVIEW OF SCIENTIFIC AND TECHNICAL LITERATURE ABOUT LIQUID DEPOSITION TECHNOLOGIES**

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NATURE OF THE DELIVERABLE

| | | |
|----------|---------------------|--|
| R | <i>Report</i> | |
| P | <i>Prototype</i> | |
| D | <i>Demonstrator</i> | |
| O | <i>Other</i> | |

**D1.2 – SUMMARY**

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| Keywords | Additive layer deposition process for sealed CCM; high-speed CCM manufacturing process with high-volume throughput; materials utilisation and quality; lamination and seal addition process; PEMFC |
| Full Abstract (Confidential) | <p>The market for PEM fuel cells will increase to 10's GWs per annum from 2015. For the catalyst coated membrane (CCM), a critical stack component, continuous manufacturing processes are currently being implemented by manufacturers worldwide. Whilst these will meet CCM demand for the next 10 years, the growing requirement for increased numbers of CCMs thereafter necessitates a manufacturing step-change, both in terms of cost and capacity. An additive layer manufacturing (ALM) process for the edge-sealed CCM is the ultimate scope of MAMA MEA consortium. The key CCM components (anode and cathode catalyst layers, ion-conducting membrane and edge seals) will be deposited with high precision and speed, one component layer on top of the other, and just in the areas of the CCM where they are required for functionality. The present document consists of a detailed review of printing and coating techniques currently available and of interest for the consortium's activities. Notably, inkjet, gravure, screen printing, spin coating, sip coating, tape casting, spray coating, slot die coating and bar coating are analysed in terms of process, physical and rheological characteristics of the inks to be employed, output quality, roll-to-roll capability and applicability to mass production. Moreover, a number of dedicated patents are also included to assess the proprietary information about these techniques within the fuel-cell manufacturing sector.</p> |
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D1.2 – REVIEW OF SCIENTIFIC AND TECHNICAL LITERATURE ABOUT LIQUID DEPOSITION TECHNOLOGIES

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NOMENCLATURE

| | |
|--------------|---|
| ALM | Additive Layer Manufacturing |
| c | concentration [g cm^{-3}] |
| CCM | Catalyst Coated Membrane |
| CIJ | Continuous inkjet |
| DOD | Drop-on-demand |
| GDL | Gas Diffusion Layer |
| kp | Pick-out ratio |
| MEA | Membrane Electrode Assembly |
| N | Number per unit area [cm^{-2}] |
| OEM | Original Equipment Manufacturer |
| PEMFC | Polymer Electrolyte Membrane / Proton Exchange Membrane Fuel Cells |
| PEI | Polyethyleneimine |
| PEN | Polyethylene naphthalate |
| PET | Polyethylene terephthalate |
| PFSA | Perfluorosulphonic acid |
| PTFE | Polytetrafluoroethylene |
| t | Thickness [mm] |
| TEM | Transmission Electron Microscopy |
| V | Volume [cm^3] in Eq. (1), volume per area [$\text{cm}^3 \text{m}^{-2}$] in Eq. (2) |

Greek symbols

| | |
|----------|---|
| γ | Surface tension [N m^{-1}] |
| ρ | Density [g cm^{-3}] |
| μ | Viscosity [$\text{Pa}\cdot\text{s}$] |
| ω | Angular velocity [$^\circ \text{s}^{-1}$] |

Subscripts

| | |
|---------------|---------|
| d | droplet |
| screen | screen |



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1. INTRODUCTION

MEA embodies the core of PEMFC in terms of both single cells and stacks. Notably, MEA performance affects overall stack efficiency, stability and durability [1-3]. As a direct consequence, its cost represents the larger share within the fuel-cell stack total [2]. Since fuel cells are expected to steadily increase their competitiveness over the next 5 – 10 years [2], especially in the automotive sector, MEA manufacturing is a current critical target: improving the related processes and technologies has become instrumental in making fuel-cell high-volume production viable and economically sustainable. However, this objective may be achieved without deteriorating stack quality (i.e., performance, efficiency and lifetime). For instance, state-of-the-art MEA employed for mobile applications have shown the capability of surviving 3,000 – 5,000 h drive cycles throughout stack testing at various power densities [3] and these values are expected to be set as a minimum threshold for OEM within the commercialization of fuel-cell-powered fleets. Similar durability levels have been also applied to MEA for stationary applications, where about 20,000 h continuous operation currently identifies an average lifetime expectation [4-8].

One of the keys to produce high-quality MEA at lower costs is to implement advanced manufacturing techniques into electrode generation, thus enabling reduction of raw-materials consumption by smart catalyst deposition, higher automation and mass production [9]. This objective can be attained by a controlled and improving cross synergy between fuel-cell and other industry sectors, particularly those where similar performance requirements are demanded. As described in the seminal review by Krebs [10], the same approach has been followed in fabrication of polymer solar cells: printing and coating techniques typical of areas like ceramic-tile or electronics manufacturing have been successfully applied and adapted to production processes. The need for forming an ink film containing catalysts onto a substrate – usually, but not exclusively, the membrane in fuel-cell manufacturing – holds for both solar- and fuel-cell industry, so as the quest for making this deposition as controllable, effective and automatized as possible. Therefore, the possibility to switch from traditional deposition techniques to innovative ones is presented in this work: the conventional hot-pressing approach [11] is reviewed towards an assessment of strengths and weaknesses; additive layer manufacturing [12], gravure coating [13] and printing techniques (i.e., screen [14] and inkjet printing [15]) are described with relation to catalyst deposition requirements and conditions typical of MEA manufacturing.

The assessment of characteristics and applicability of each considered technique should ultimately serve as a guidance for scientists and engineers towards improving catalyst deposition in PEMFC electrode fabrication. Figure 1.1 shows a schematic of a single-cell design: MEA (with catalyst layers), GDL, seals, gaskets and bipolar plates and Figure 1.2 shows Microscopy snapshots of N772 carbon black [16].

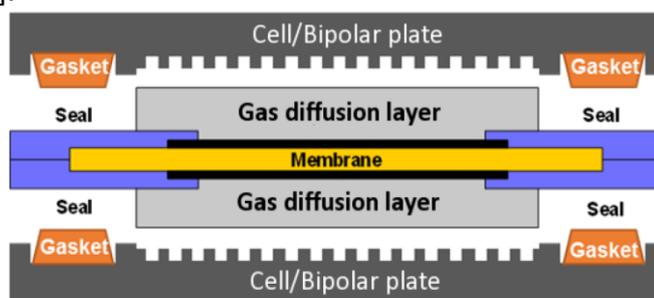


Figure 1.1. Schematic of a single-cell design: MEA (with catalyst layers), GDL, seals, gaskets and bipolar plates

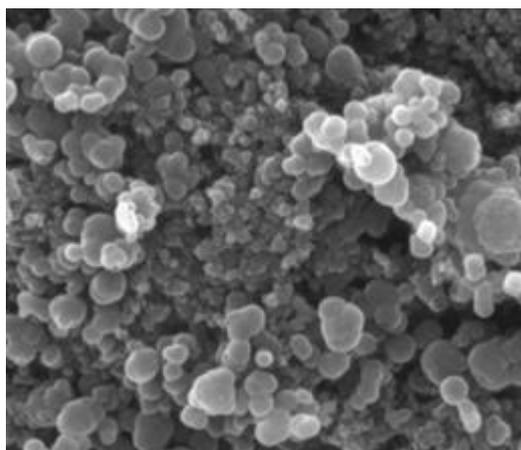


Figure 1.2. Microscopy snapshots of N772 carbon black [16]

2. LAYER AND SUBSTRATE CHARACTERISTICS

Fuel cells and particularly PEMFC can be represented by technical sketches as that of Figure 1.1., where all the components involved in single-cell operations are included. Some of them fall beyond the scopes of the present work: bipolar plates, mainly for hydrogen and air distribution [17]; GDL for promoting reactant diffusion across the CCM [19]; gaskets/spacers for preventing gas leakages and allow suitable compression. As mentioned in the previous section, this review is focused on the CCM as the substrate and on the deposition of catalyst layers. Seals are an additional subject as they are in direct contact with both the membrane and the catalyst layers.

Catalyst layers are the core of this work, since they constitute the actual electrodes, to be deposited onto a substrate. Currently, most commercial catalyst layers used for PEMFC are constituted by Pt-based catalysts supported by nanoparticulate carbon black. Deposition is typically performed through an ink, which is formed by mixing the catalyst compound with a perfluorosulphonic acid ionomer; the mixture usually appears as a stable suspension in suitable solvents. The ink structure and ability to coat the substrate upon impact onto the surface are largely driven by the carbon-support morphological features. Notably, the ink mainly consists of small (10 – 100 nm) primary particles that physically combine with each other and form aggregates; those aggregates represent the smallest chemical unit that can be generated out of carbon black. Typically, aggregate size spans from 100 nm to 1 μm : the lower end of the range results from the rupture of larger, micrometric agglomerates into basic aggregates during the operations of ink preparation [20]. As in early works [20], TEM has been successfully employed to emphasize the degree of coagulation between particles. Figure 1.2 shows an image with the primary building blocks and highlights a typical high structure that translates into higher coagulation. Typical commercial carbon black is used at the anode (e.g., Cabot Vulcan XC72R, Akzo-Nobel Ketjenblack EC-300J); at the cathode, specifically modified carbon-black-supported catalysts may be advised towards a higher corrosion resistance with respect to commercial carbon black. Moreover, high resistance to Pt sintering [3] is also recommended at the cathode. It is noteworthy to clarify that Pt loading on carbon black is typically 50 wt% of the whole catalyst and consists of 2 – 5 nm particles attached to the carbon-black particle surfaces. However, and in spite of the almost equal portion, ink and coating properties are mainly governed by the carbon-black structure, as previously mentioned.

In PEMFC, the membrane is the substrate into which catalyst deposition is usually performed, thus building the electrodes; it consists of a thin (15 – 20 μm for stationary [6,7] and 10 – 20 μm for mobile applications [2,3]), ion-conducting polymeric film. Notably, the film is made up by a 2-component composite material [21]. One of the 2 is the ionomer material, which includes a PFSA. The molecule has the typical sulfonic-acid structure with $-\text{SO}_3\text{H}$ groups providing proton conductivity. The acid groups are attached to the ends of pendant C-F chains [22], so the polymer is *de facto* separated over a conductive and a non-conductive phase. As in the commercial Nafion[®]-based membranes [22,23], this characteristics emphasizes both relative conductivity and strength, mostly through the highly functional nature of the ionomer. The ionomer ion-conductive property is strongly governed by the ionomer processing; notably, the solvents used to disperse the ionomer and the heat treatment are the predominant parameters and mechanisms in determining the ionomer microstructural features [24]. As the second component, a reinforcement material is integrated within the membrane; usually a polymer, it typically consists of an expanded PTFE film. Thanks to the carbon-fluorine bonds, it improves the membrane mechanical strength, also acting against significant dimensional changes due to repeated hydration/dehydration cycles. From a manufacturing standpoint, membranes are produced by casting multiple layers of the ionomer dispersion one on top of the other; the reinforcement material is then added to the central layer of the batch. Once finalized, the membrane appears as a thin, solid roll supported by a thicker carrier film.

An additional component of interest for the present work, the seals for PEMFC are currently made up by composite films including an adhesive (heat- or pressure-sensitive) layer. A solid polymer film is also added to increase their mechanical strength. As previously mentioned, the adhesive layer lies in direct contact with the catalyst layer and/or the membrane during cell operations, so its chemical stability in an acidic environment has to be particularly high. Moreover, seals may be able to tolerate the PEMFC operating temperature with no perceivable deterioration of the mechanical properties. Notably, the polymer film operates in contact with the gasket, thus requiring a high mechanical strength.

Typical polymer films used for seals are PET, PEI and PEN. The overall seal thickness is usually between 15 and 50 μm , where the relative thickness and distribution of adhesive and polymer film may vary upon CCM design and operating conditions.

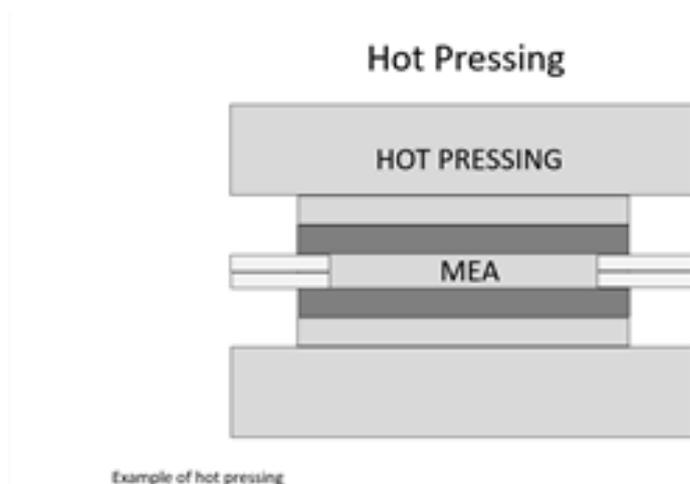


Figure 2.1. Schematic of a hot pressing used for a MEA [17]



3. STATE-OF-THE-ART MANUFACTURING OF COATED MEMBRANES

Conventional CCM manufacturing process consists of: ink deposition – catalyst and ionomer included – to form the catalyst layers onto decal-transfer carrier films; heat- and pressure bonding against the membrane (after removal of the membrane support film); decal-transfer carrier film removal. As mentioned in Section 2, seals are finally applied to the CCM: a frame of seal film material is pressed or heat-pressed onto the substrate surface Figure 2.1. As highlighted in the introduction (Section 1), PEMFC manufacturing is shifting from low-volume batch (also known as discrete-part or singulated-part) processes to high-volume. In the former, multiple discrete-part MEA are laid for bonding in multi-daylight static presses, whereas in the latter a continuous roll-to-roll process is carried out. There is a general lack of technical and scientific literature on the CCM and MEA manufacturing processes being developed worldwide by competitive developers, since they tend to avoid disclosing details about their production lines [12,25]. In particular, it appears to be very little disclosure of additive layer processes for CCM manufacture, and certainly no disclosures of a sealed CCM made by such processes. However, there is a reasonable number of patents on various applications filed for PEMFC CCM and MEA manufacturing [26,27], see chapters 10 and 11.

The early studies of the late 1990s focus on the basic continuous CCM production process, involving heat/pressure transfer of preformed catalyst layer films to a continuous membrane film [28]. In 1997, Bönsel et al. [29] claimed a continuous process for laminating a centrally arranged membrane with catalyst layers either side. Later, Ripley et al. [30] obtained a patent on a specific process step for the addition of a continuous seal window to a continuous strip of CCM, based on the general process outline described above. The patent by Debe et al. [31] deals with the applications of a continuous roll-to-roll CCM process for automated fabrication of multiple layer fuel cell assemblies, including gaskets and MEA in roll good form.

In the current hot-bonding manufacturing process of CCM, each of the 3 main components is deposited onto a separate carrier film, a consumable material as it is destroyed during the processing, used to support the component through the process. Once all of the separate components have been produced, they are bonded together using heat in a flat-bed press or more recently in a continuous process using a roll-to-roll lamination system. A fine balance heat-pressure is required in the process: too much heat and pressure and the materials are damaged, too little and a poor lamination is achieved. Successively, the seal windows are applied, also by heat and/or pressure. The last step is the cutting of the CCM to their final dimensions.

During hot-lamination, the ionomer in the membrane and the ionomer material in the catalyst layer structure are in direct and firm contact to minimize the resistance to proton transfer across the interface. This contact also ensures a good mechanical bond between the layers preventing the layers from de-bonding during operation. During the process, this interface can be subject to significant high stress as the membrane changes dimensions due to its water content: the heating can cause excessive water loss from the membrane that causes it to shrink and affect the performance achieved by the CCM.

An important feature of the current roll-to-roll CCM process is that it is a continuous process in which the hot-lamination step occurs between 2 heated rollers. Additional heat can be introduced by preheating the materials; this can cause issues to any unsupported membrane materials as they will dry out and as a result their dimensions may change. Therefore, an extensive know-how of these processes is required to produce high-quality CCM materials.

Another significant issue of the current roll-to-roll CCM process is that the key materials utilization (being around only 70-80%) is not fully optimized. In the current CCM designs application of certain



CCM materials is not confined to the active layer of the CCM where it is functionally required: the membrane and the catalyst layers extend beyond this to provide a surface onto which the seals window can be applied. This is an inefficient use of the most expensive CCM components. The carrier film, on which each individual component (the 2 catalyst layers, 2 seal windows and the membrane) are supported, is removed during the lamination and conversion process, and finally discarded. If the membrane terminates under the seal region, the seals have to conform around the membrane: a small air gap may form in the region at the edge of the membrane and this can be an issue, as it offers a pathway for gas leakage and can be filled with water from the membrane. Sometimes this water can freeze and mechanically damage the membrane-seal interface.

A third feature of the current roll-to-roll CCM process is that the CCM designs can lead to more prevalent instances of crack defects and quality issues prone to affect the manufacturing yields obtained. In particular, in the hot-lamination step, the membrane is taken above its glass transition temperature, it loses a part of its mechanical properties and can be seriously damaged.

As a result, from all the previous considerations, it appears there is a need of specific dimensional designs imposed by the stack developer of the CCM to reduce or even eliminate the above described features: these issues can impact negatively on overall CCM costs. Whilst the current-state-of-the-art CCM process has some challenges to overcome, solutions are being developed to find a viable solution in the short to medium term for the fuel cell industry. In addition, due to the growth in the volume of CCM that will be required from 2025 onwards, alternative processes are identified and evaluated to satisfy the increased demand effectively.

Recently, Gore[®] – one of the leading supplier of MEAs and membranes for the PEM fuel cell industry – has investigated the use of an additive layer CCM in a project with US Department of Energy [32]. The preliminary results of the project, show the capability of producing 100 linear meters. However, further optimization of the process is necessary. Ghielmi et al. [33] have been recently granted a patent on a method for the preparation of integral catalyst-coated membranes for use in PEMFC.

4. PRINTING TECHNIQUES

Printing could be described as the materialisation process of data (e.g., images, text, graphics, patterns) by applying ink onto a substrate with the help of a printing plate (master) for conventional printing as well as master-less process for the digital and non-impact printing. The following scheme in Figure 4.1 shows the most used printing technologies for the production of printed products variations [34].

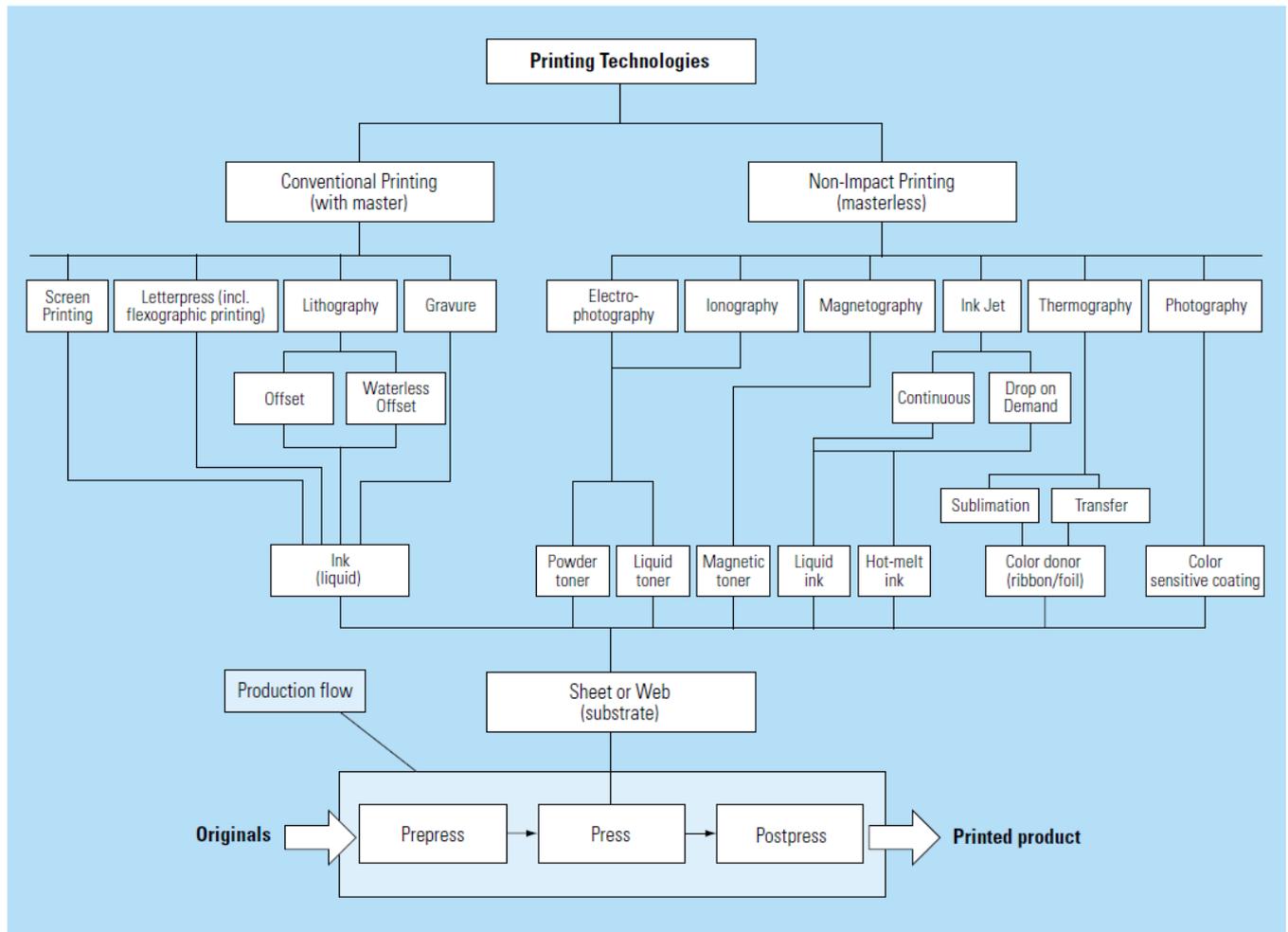


Figure 4.1. Scheme shows the most used printing technologies for the production of printed products variations. [34]

In order to choose the most suitable printing technology for CCM production, many parameters should be considered. The following sections focus on the most promising printing techniques which are widely used in the production of printed electronics. These technologies are inkjet, gravure and screen printing.

4.1. OVERVIEW OF INKJET TECHNOLOGY

Inkjet is a non-contact deposition technique. It progressively builds up the printed pattern directly onto the substrate by the deposition of many individual, tiny drops of ink [35-51]. Each

droplet, typically 10 – 100 μm in diameter, is created and deposited under digital control. Inkjet printing has continued to evolve in recent years and to become more widely employed in a range of industries. As shown in Figure 4.1., the main technologies in use in contemporary inkjet printers are 2: continuous (CIJ) and drop-on-demand (DOD) inkjet. In Figure 4.2. the schematics of the principle of the main inkjet printing methods (i.e., (a) continuous inkjet (CIJ), (b) drop on demand (DOD) thermal inkjet and (c) (DOD) piezoelectric inkjet) are shown [73].

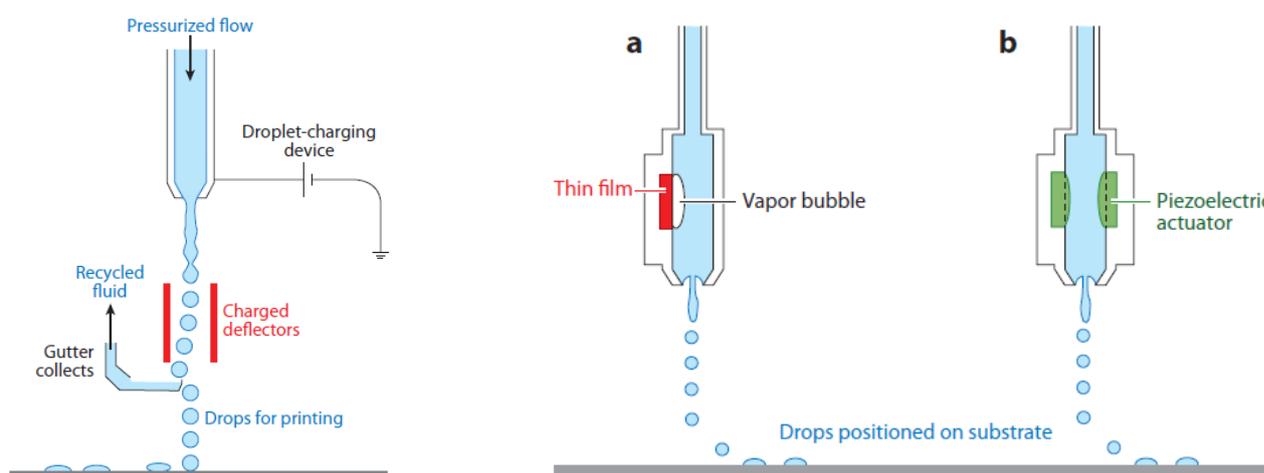


Figure 4.2. Schematic shows the principle of the main inkjet printing methods e.g. (a) continuous inkjet (CIJ), (b) drop on demand (DOD) thermal inkjet and (c) (DOD) piezoelectric inkjet. [73]

In CIJ a continuous stream of ink droplets is created by a piezoelectric system. The droplets are subjected to an electrostatic field created by a charging electrode as they form; the field varies according to the degree of drop deflection desired. This results in a controlled, variable electrostatic charge on each droplet. The charged droplets pass through another electrostatic field and they are directed or deflected by electrostatic deflection plates to print on the substrate or allowed to continue undeflected to a collection gutter for re-use. In DOD the droplets are created on demand by a piezoelectric crystal or a heating element. The use of that technique offers many benefits e.g. the ability of printing specific and well-defined areas, the use of large ink volumes, the micrometric-scale particle size depositions onto substrates and the high resolution printed products.

The dry thickness t of a printed layer is a function of the number of droplets delivered per unit area N_d , the volume of each individual droplet V_d and the concentration of solid material within the ink c [10]. It can be quantified by the following expression:

$$t = N_d \cdot V_d \cdot c / \rho \quad (1)$$

where ρ is the density of the material in the deposited layer.

Inkjet is used in several industrial process: electronics, decoration of textiles, ceramics, food, and life sciences applications [40]. In particular, the use of inkjet printing technologies in manufacturing of printed electronics devices is widely increasing. For instance, it is used for the production of organic photovoltaic (OPV) [37 - 39], organic thin film transistors (OTFT) [41], printed batteries [42], radio-frequency identification (RFID) antennas [43], capacitors [44], low pass filters [44], pressure sensors [45], organic light emitting diodes (OLED) [46], electrical components on different materials [47].



Application of inkjet printing for CCM fabrication has shown a particular progress since its initiation in 2007 [35,36]. It has the potential of being a technique suitable for PEMFC CCM products, specifically for the catalyst layer deposition. Inkjet printing has been demonstrated at laboratory scale on small active area cells, with generally low catalyst loadings i.e. Pt loading for the cathode was 0.25 mgPt/cm^2 and for the anode was 0.05 mgPt/cm^2 , which have been tested for short periods of time [49].

The technique presents some very clear advantages compared to other methods: improved ink utilization with respect to spraying, reduced waste due to an environmentally friendly process with lower energy use, decreased relative costs and significantly increased printing quality as a result of its extremely high resolution (at least 300 dpi, potentially up to 1,200 dpi [10]). The non-impact inkjet deposition process also allows applying onto fragile substrates. As all digital printing methods, it is one of the most suitable choices for short runs, variable data and just in time printing.

The flexibility of controlling the Nafion[®] and Pt-loading distribution in the catalyst layer is much higher than that with other deposition methods. Moreover, inkjet printing allows the fabrication of thin, low-loading electrodes and functionally-graded layers. Inkjet printing generally permits a fast set-up time and changeover to a new part design, which does not require new tooling, thus reducing costs and increasing flexibility and batch sizes.

The development of inks with the necessary functional electrochemical and rheological requirements is of key importance. The ink must be stable in time with a maximum dispersion of aggregate particle sizes are generally lower than 1/100 of the nozzle print head diameter [58]. In practice and under certain circumstances, it is possible to deposit inks with relatively bigger particle sizes up to 1/10 of the nozzle print head diameter [59].

4.2. PRINTABLE/TYPICAL RANGES AND CHARACTERISTICS OF INKJET INKS

In order to choose the right ink for inkjet process, several parameters should be considered e.g. particle size and loading, viscosity, ink density, vapour pressure of the solvents, aggressive or dangerous solvents (health), contact angle and surface tension.

These parameters are of importance for the printing/drop formation (ideal spherical drops and no nozzle clogging) as well as for the wetting and layer formation on the substrate (no de-wetting, no or minor coffee-ring-effect)

- Viscosity, density and surface tension

The theoretical Z number determines the printability of fluids. It is based on Reynolds number and Weber number. While Reynolds number (Re) is the ratio of inertial forces and viscous forces, Weber number (We) is the ratio of inertial forces and surface tension forces [64, 68, 66]. Z number is a dimensionless number which represents the relation between ink density ρ , viscosity μ and surface tension γ [64, 68, 66].

$$Z = \frac{\sqrt{(\gamma\rho L)}}{\mu} \quad (2)$$

L: typical dimension (orifice radius), ρ : density, γ : surface tension, μ : dynamic viscosity [67]

- (1 < Z < 4): long tail, long time to single drop, degraded positional accuracy
- (4 < Z < 14): satellite drop, merging with main drop after 140 to 180 μs → ideal drop
- (14 < Z): easy droplet ejection, no significant viscous dissipation, satellite drop [62]

Figure 4.3 shows the Reynolds-Weber number space, with the region of fluid properties where inkjet drop formation is optimized [56][57].

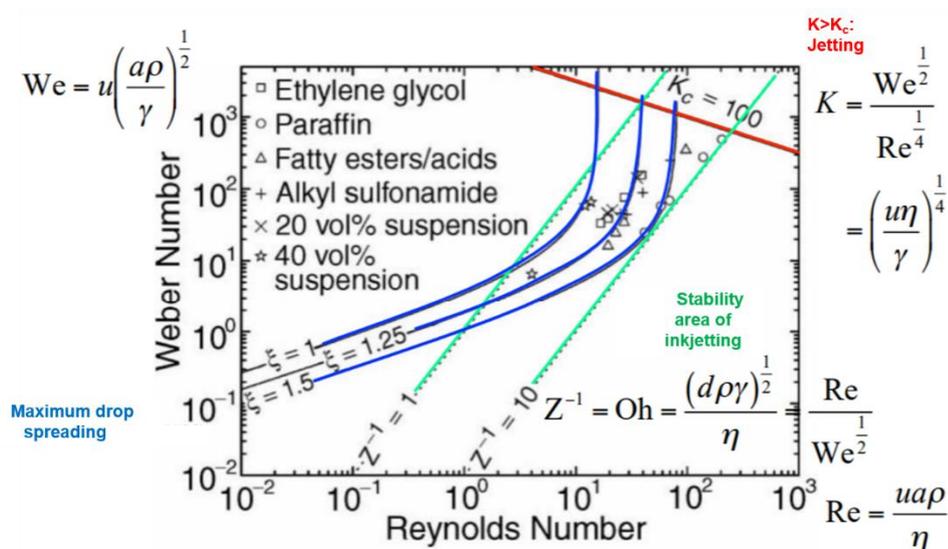


Figure 4.3. Representation of Re - We parameter space with the region of fluid properties where inkjet drop formation is optimized (private communication from Prof. Winterer [56])

- Particle size and loading

The particle loading in the ink is closely related to the particle size. The use of bigger particles will lead to a higher possibility of clogging the nozzles. In other words, it is recommended to decrease the particle loading for the use of bigger particles → otherwise clogging of nozzles.

For instance, the maximum particle size should not exceed 1/100 of nozzle diameter [58].

The nozzle diameter is different from one machine and one print head to another. For instance, Fujifilm Dimatix offers the DMP 2831 with the orifice radius of approximately 21.5 μm (DMC-11610 print heads), as well as Fujifilm Dimatix DMP 3000 with orifice radius of approximately 42 μm (SE3 print heads).

- Vapour pressure of the solvents, aggressive or dangerous solvents (health)

The solvent should not evaporate immediately, otherwise this can lead to nozzle clogging. It should also not evaporate too slowly, to avoid excessive spreading (no sharp edges)

Typical solvents for inkjet printing (e.g. single or mixture of several solvents, based on common inkjet inks used in TUC labs): Ethanol, Triethylene glycol monoethyl ether, 2-(2-butoxyethoxy) ethanol, Tripropylene glycol mono methyl ether (TPM). Additionally, Diethylene glycol, Ethylene glycol, 2-Propanol, Butanol, Dimethyl sulfoxide, Glycerin; 1,2,3-Propanetriol, Ethyl acetate are used.



- Contact angle

The contact angle is very important and characterising the wettability of an ink onto the substrate (hydrophobic or hydrophilic) [62]

The contact angle is a measure of the spreading of a liquid (ink drop) on a substrate. It is defined by the surface tension of the solvent as well as the surface energy of the substrate → solvent-substrate interaction. On a hydrophilic substrate with very low contact angle, the ink tends to spread more. On a hydrophobic substrate with high contact angle, the ink spreads less. The contact angle should be below 90 ° to ensure a proper layer formation [62]

The following table shows various examples from literature for the basic requirement for inkjet inks

Table 4.1. Basic requirements for inks in inkjet printing

| | |
|------------------|--|
| Z number | $1 < Z < 14$ [62,65] |
| Viscosity | $< 20 \text{ mPa s}$ [63] |
| Surface tension | $< 80 \text{ mN.m}^{-1}$ [63] |
| Particle size | $< 1/100$ to $1/10$ of nozzle diameter [58] [59] |
| Particle loading | 10 – 70 wt% [60] |
| Contact angle | $0^\circ < \theta < 90^\circ$ [62] |

5. GRAVURE PRINTING

5.1. GRAVURE PRINTING TECHNIQUES

Gravure printing technique is considered one of the most productive traditional printing methods. The printing plate is commonly made of metal in form of a cylinder for the long run and mass production processes e.g. steel base cylinders coated with copper [34]. Another examples is the use of silicone based cylinders for special applications e.g. production of tile ceramics. The image elements in gravure printing are engraved into the surface of the printing plate (e.g. metal cylinder) forming the printing pattern within cavities, called “cells” [34]. The non-image areas are the remaining areas of the cylinder surface which are not engraved and they are on the same level of the original plate surface [34]. The printing process starts by flooding both image areas and non-image areas with the low viscosity gravure ink. Afterwards, the cylinder is wiped with the so called doctor blade to remove the ink from the upper surface of the plate and the ink remains only in the lower cells. With the help of an impression cylinder, the ink transfers form the engraved cells onto the substrate with the adhesive force between ink and substrate. Meanwhile, the impression cylinder uses high printing pressure allowing easy transfer of the ink onto the substrate [34].

Gravure printing permits to obtain images with very high quality and layer-thickness homogeneity. It is used for large volume, high-quality printed products such as periodicals, magazines, carrier bags, catalogues, packaging, security paper and many other applications. Figure 5.1 shows a schematic of the principle of gravure printing method [34]

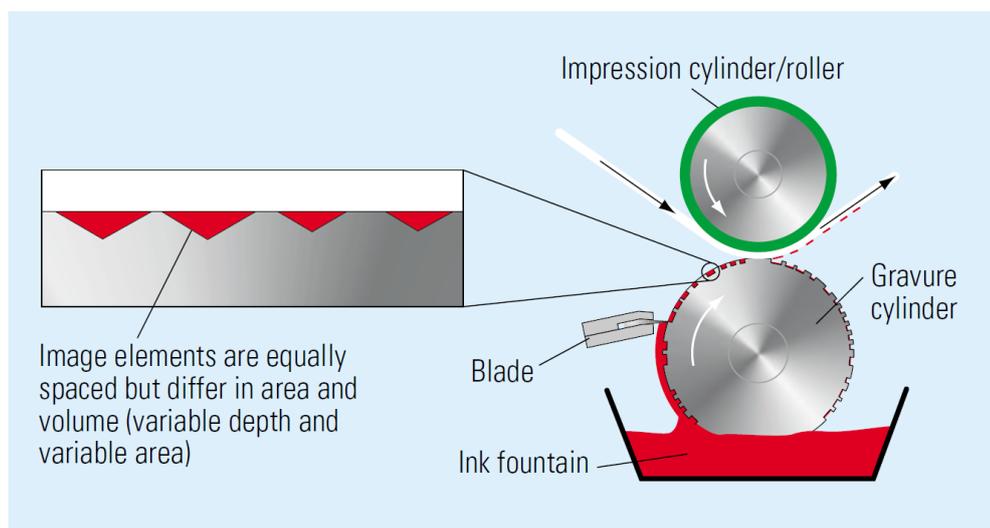


Figure 5.1. Schematic shows the principle of gravure printing method. [34]

5.2. PRINTABLE/TYPICAL RANGES AND CHARACTERISTICS OF GRAVURE INKS

The inking unit of a rotary gravure printing system consists mainly of an ink reservoir and a doctor blade system directly supplying the printing cylinder with ink. Therefore, it is considered as the shortest inking system compared to the other traditional printing techniques. The ink transfers firstly from the ink fountain onto the printing plate, is levelled by the doctor blade and consequently deposited onto the substrate. This process requires low viscosity liquid inks in the range of 10 to 200 mPa s, [34][69]. For a successful ink transfer in gravure printing process, a few conditions should be considered: ink rheology, machine speed, solvent evaporation rate, gravure cell geometry, doctor blade wiping force and angle, pattern layout and type of substrate [70]. For instance, high speed printing and absorbent substrates require lower viscosity inks.

- Ink formulation

For colour printing gravure ink could be formulated using the following components [70]

- Pigment (Functional material) 4- 12%
- Extender 0 – 8 %
- Resin 10 – 30 %
- Solvents 40 – 60 %
- Additives 2 – 10 %

- Choice of solvents

The right choice of the solvent plays an important role in transporting the solid ink particles from the ink fountain to the substrate through Gravure inking system [71]. Therefore, many parameters should be considered e.g. work safety, evaporation rate, boiling point, flash point and explosion limit. Typical solvents for gravure printing are ethanol (ethyl alcohol), ethyl acetate (acetic ether)



and water (mainly mixed with other solvents e.g. alcohol for better substrate adhesion). Meanwhile, in order to extend the applications of gravure printing, more solvents could also be used under certain safety precautions, e.g. toluene and xylene [34].

- Contact angle

Contact angle (θ) should be in the range of $0^\circ < \theta < 90^\circ$ ensuring proper layer formation [72].

- Particle size

In gravure printing larger particles compared to inkjet could be printed with less printing defects and less damage to the printing system. Nevertheless, particles greater than $75 \mu\text{m}$ will cause defects e.g. stripes, dark inking spots, scratches and staining the printed pattern [71]. Therefore, it is recommended to have particles of size in the order of $10 \mu\text{m}$ or smaller to decrease printing defects and to extend the life time of the gravure cells and the doctor blade [71].

The following table shows examples from literature for the basic requirement for gravure inks

Table 5.1 Basic requirements for inks in gravure printing

| | |
|---------------|--|
| Viscosity | 10 to 200 mPa s [34,69] |
| Particle size | $< 10 \mu\text{m}$ is recommended [71] |
| Solid content | (Particle loading wt%) \propto (η Viscosity) |
| Contact angle | $0^\circ < \theta < 90^\circ$ [62] |

6. SCREEN PRINTING

In screen printing Figure 6.1., the ink, or screen printing paste, in the form of a highly viscous fluid is poured onto the top of a screen fixed to the edges of a frame. The meshes of the screen are open or closed, respectively, according to the pattern of the image layout. The ink can pass only through open areas to form the required image. The substrate is positioned underneath the screen while a suitably shaped squeegee is drawn across the upper surface of the screen forcing the ink to pass the screen and deposit onto the substrate. The wet thickness of the deposited layer is theoretically coincident with the paste volume of the screen V_{screen} , actually the ink volume per area of open screen and meant as the amount of ink contained within the threads of the mesh through the emulsion thickness [10,53]. However, numerous parameters may affect deposition effectiveness like pushing force applied to squeegee, hardness and shape of squeegee, snap-off distance (i.e., the distance between the squeegee at its final, horizontal position and the screen flat surface), or the speed of the squeegee upon activation. So, the dry thickness t of the film deposited onto the substrate may result from including partial deposition of the ink through the pick-out ratio k_p [10,53], which can be governed by varying the parameters previously mentioned:

$$t = V_{screen} \cdot k_p \cdot c/\rho \quad (3)$$

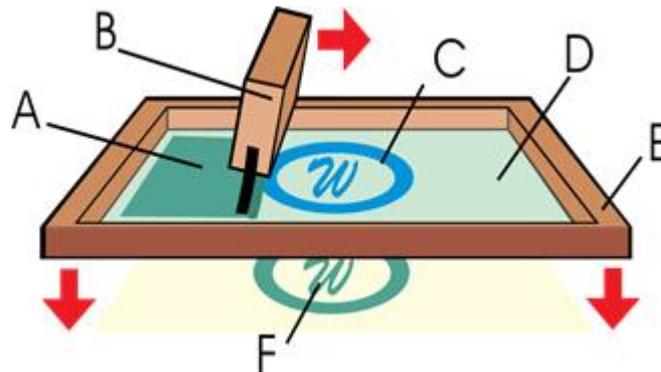


Figure 6.1. Sketch of screen printing method: A. Ink. B. Squeegee. C. Image Pattern. D. Photo-emulsion. E. Screen support frame. F. Printed image [52]

where concentration c is that of the solid material within the ink and density ρ refers to the material in the deposited layer and V_{screen} refers to the theoretical paste volume of the screen.

Alongside gravure printing, screen printing is widely used in the field of printed electronics as well as graphic printing. This technology is well-known from the field of printed circuit boards, where it has been employed for several decades to deposit conductive pastes. In comparison to gravure printing, screen printing is a less accurate process because the feature sizes of the printed lines, etc. are quite high resulting in low print resolution. However, the process allows the transfer to high material volumes and large particles, if required, enabling the production of high layer thicknesses.

Flatbed screen printing is relatively slow and a roll-to-roll process may be needed if applied to mass production. Figure 6.2 shows a schematic diagram of the rotary screen printing. Similar to traditional screen printing the paste is forced through holes of a rotating drum in a screen using a rubber squeegee and the coating material flows through open areas perforating a thick printing substrate [83]. Figure 6.2 shows a sketch of the rotary screen printing [54].

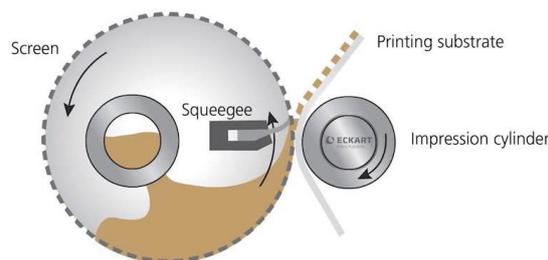


Figure 6.2. Sketch of rotary screen printing [53]

Contrary to flatbed screen printing, rotary screen printing has the advantage of continuous operation. Thus, the opportunity to increase production speed is given, particularly for substrates printed on a web. In screen printing usually the inks have higher viscosity therefore very often in the literature they are referred to as paste. Therefore, the ink is exposed to atmosphere for extended periods of time and thus volatility of the solvent is critical for the process. To ensure sufficiently slow drying, slow evaporation rate carrier fluids such as pine oil or other binders are used. The choice of



binder is as important as the choice of solvent. The binder merely contributes to the overall rheological properties of the paste.

Typical single layer thickness achieved by screen printing is between 10-30 μm and multi layers up to 200 μm can be reached. The viscosity range for optimal performance lies between 1-10 Pa s. The inks should possess shear thinning behavior and this property gets more important for finer mesh structures. In comparison to other printing methods, particle loading in screen printing is relatively high and ranges between 10 and 40 vol%.

Gravure and screen printing are arguably the most promising conventional printing methods in the wide area of functional printing (e.g., printed electronics) [15,34]. They are considered as very robust and sustainable technologies for industrial applications that require high material throughput, high homogeneity and positional accuracy. They offer significant prospects for the greater cost reduction and quality improvements that are required by the fuel-cell industry as it moves towards mass production.

7. COATING METHODS

7.1. SPIN COATING

Using a spin-coating, very thin and uniform coatings can be created. At the beginning of the process, a portion of an ink is deposited onto the center of a stationary or slowly rotating substrate (deposition). The substrate is then accelerated to several hundred rotations per minute giving rise to centrifugal forces (spin-up). During this step, adhesion forces between the substrate and ink oppose the centrifugal forces which give rise to a shear force in the fluid and a rapid ejection of the fluid. At this stage the rotation of the substrate would reach even higher (typical 2000 to 5000 rotation per minute). This leads to further uniformity and thinning of the film (spin-off). Finally, the films dry and the solvent leaves the substrate. It is important to mention that evaporation occurs during all stages. All the stages of spin coating are shown in Figure 7.1 [74].

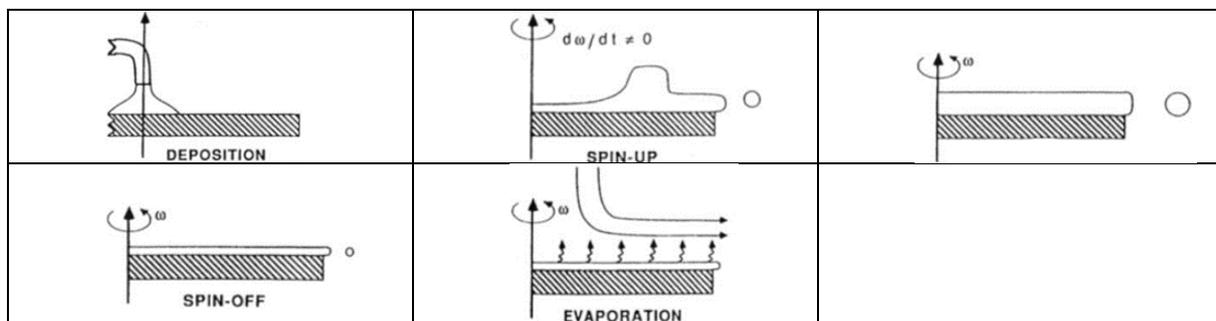


Figure 7.1. stages of spin coating (from left to right; first row, then second). [74]

The final film thickness h can be calculated from the formula:

$$h \propto \left(\frac{e\eta_i}{mf_s\rho_i\omega^2} \right)^{1/3} \quad (4)$$

where mf_s is the mass fraction of solvent in the ink, ω is the angular velocity, and ρ_i , η_i , and e are respectively density, viscosity, and evaporation rate of the ink, respectively. By adjusting the angular velocity during the spin-off, the final thickness of the film can be adjusted. The mathematical relation for thickness evolution as a function of time and angular velocity is shown in Figure 7.2 [75].

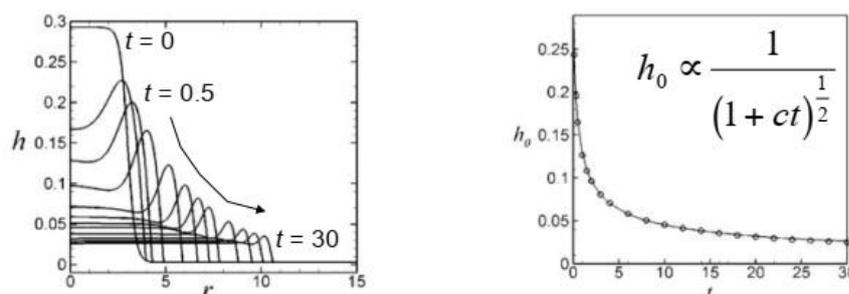


Figure 7.2. Evolution of thickness as function of time and angular velocity. [75]

Spin coating is an inefficient fabrication technique since up to 95% of the particle-loading is removed from the substrate during the spin-off. Taking into consideration the difficulty of preparing a stable dispersion, this can be an issue with toxic solvents or expensive catalytic particles. One more limitation of the spin coating is the requisite for ink to exhibit near-Newtonian rheological behavior. In a spin-coating process, the shear forces are considerably higher at the edges of the sample compared to the center. This leads to thickness anomalies for shear thinning and shear thickening inks. The former exhibits lower thickness at the edges and the latter shows higher thickness and surface defects at the edge of the sample. The typical thickness reachable with spin coating is varying between several hundred nm to 1-3 μm for single layers and is typically limited to about 50 μm for multi layers. The powder loading can be max. 20 vol% but this value is strictly dependent on density of the powder. Also the optimal viscosity for Newtonian inks in this method lies between 0.01 and 1 Pa s. [76]

7.2. DIP COATING

The dip coating process can be divided into few stages: immersion, deposition and drainage, and evaporation. It is during the drainage stage that the thickness of the wet film is defined by the balance between the viscous drag of the liquid trying to keep the film on the substrate and gravity causing it to flow off the substrate. It is a very slow process and yet it is possible to make continuous coating as shown in pictures below. Figure 7.3. [74] and Figure 7.4. [77] [74].

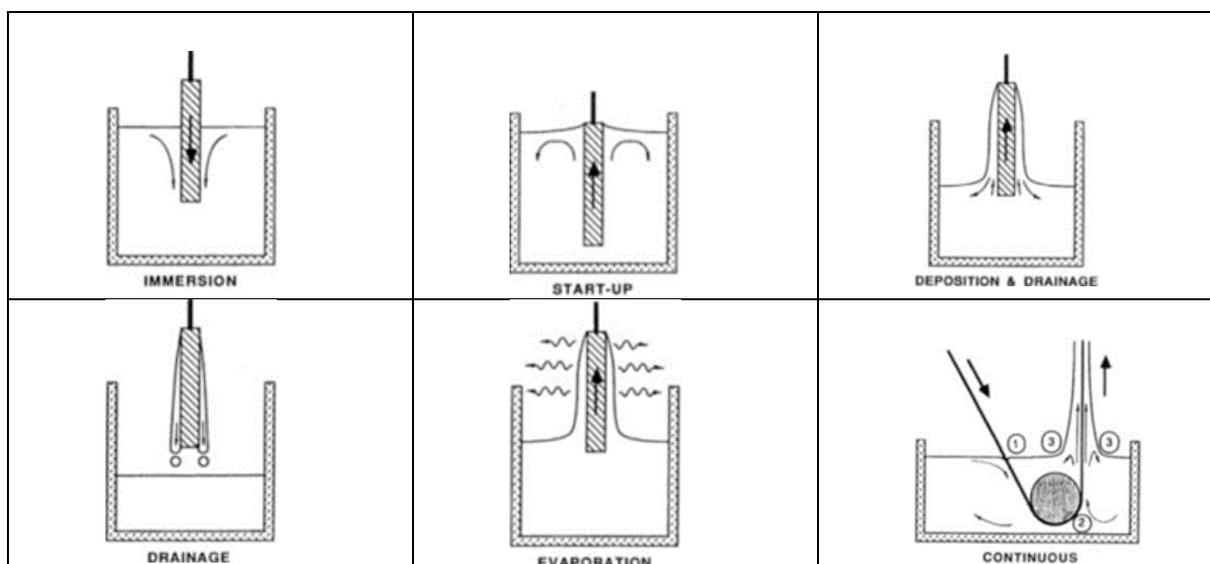


Figure 7.3. Stages of dip coating (from left to right; first row, then second) [74]

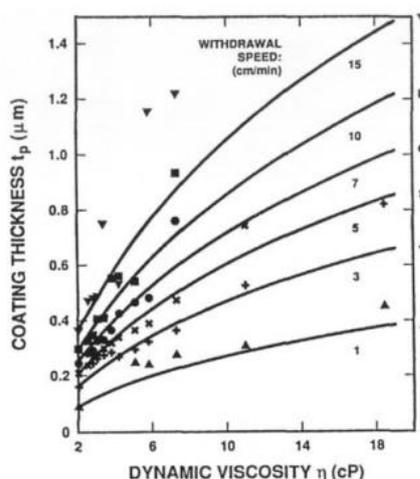


Figure 7.4. Layer thickness out of viscosity [74,77]

The layer thickness h comes out of viscous friction force and gravity and depends on the velocity of substrate and viscosity of the liquid. In the specific case of high velocity extraction, the formula requires compensation and correction by surface energy (γ_{lg}) and is presented as follows [74][77]:

$$h = 0.944 \left(\frac{\eta U}{\gamma_{lg}} \right)^{\frac{1}{6}} \left(\frac{\eta U}{\rho g} \right)^{\frac{1}{2}} \quad (5)$$

The optimal speed is very dependent on dynamic viscosity. For the desired thickness an experimental matrix is necessary that describes the thickness as function of dynamic viscosity and extraction speed Fig. 7.4. After drainage, the film undergoes further shrinkage due to the evaporation of the solvent and dripping. The thickness is therefore not only governed by the characteristics of the ink but also can lead to significant shrinkage due to the low powder loading. The final film thickness can lay between several hundred nm and 50 μm . Ink viscosity should be as low as 0.01 Pa s. Powder loading therefore cannot exceed 5 vol% (typically between 0.5-5 vol%).

7.3. BLADE/KNIFE/DOCTOR COATING – TAPE CASTING

The working principal in this method is to create a uniform film by drawing a blade across ink while maintaining a set height between the blade and substrate. For continuous and roll to roll application the substrate is moved by constant velocity and the blade is fixed at specific coordinates. The relative viscosity of the ink and blade needs to be sufficiently high, to prevent the ink from flowing out of the bottom of the reservoir in an uncontrolled manner, while being low enough that it is able to flow steadily while the substrate moves relative to the doctor blade. As shown in Figure 7.5 [78][10].

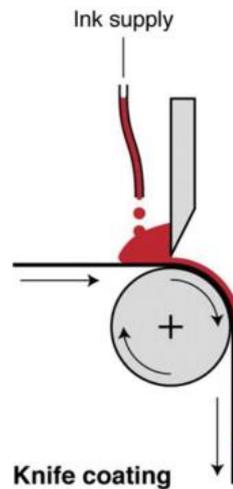


Figure 7.5. Roll to roll Knife coating [78]

The thickness of the film can be estimated by using the following formula.

$$d = \frac{1}{2} \cdot g \cdot \frac{c}{\rho} \quad (6)$$

g : gap width, c : solids content (g/cm^3), ρ : density

In a continuous process and with the assumption of non-newtonian behavior correction factors α , β have to be introduced in order to calculate the thickness of the dry film. Other factors that appear in the formula are the density of suspension ρ_w and density of dry film ρ_d , the wet film thickness (the height of the casting gap h_0 , thickness L the cutting edge, the speed of the casting head U and hydrostatic pressure difference Δp . A sketch is shown in Figure 7.6. [77].

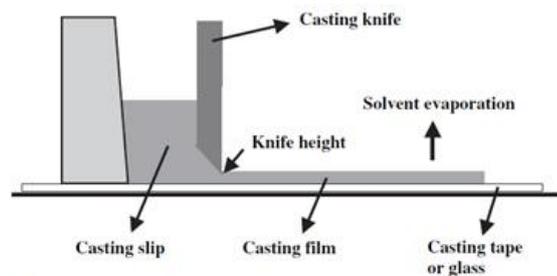


Figure 7.6. flat bed Knife coating [77]

$$h_d = \frac{\alpha\beta\rho_w}{2\rho_d} h_0 \left(1 + \frac{h_0^2 \Delta p}{6\eta UL} \right) \quad (7)$$

The typical thickness with this method is between 1 μm and 1 mm. The optimal viscosity range of the inks is 100 – 130 mPa s. Knife coating is a good method for high particle loading since it can contain up to 40 vol% of particles. [76]

7.4. SPRAY COATING

Liquid suspensions can be atomized and deposited onto a substrate to form a coating. There are various ways to atomize liquid suspensions yet the resulting layer characteristics is common to all.

Most commonly used methods are air atomizer (e.g. airbrush) and electrospray, however recently ultrasound spraying got more into focus. In the former difference in pressure between the carrier gas stream and the ink reservoir draws the ink into the stream. The ink is then broken up into small droplets. However, in electrospray, the ink is pumped through a nozzle held at a high electrical potential relative to the substrate. The ink is charged and breaks up into small droplets to transfer from a point charge towards a planar substrate at lower potential (or opposite charge). In this method the substrates are mostly conducting, but thin non-conducting substrates inserted between nozzle and conducting plates are also used.

The basic requirements of the ink are broadly similar in all spraying methods. In all cases, it requires low surface tension and it must contain high boiling solvent to be able to produce small droplets and remain liquid during the flight trajectory. If these conditions are not fulfilled this method either fail totally or the resulting film would have rough surface and defects. The typical film thickness is less than 100 μm and viscosity of the ink should not exceed 5 mPa s and particle loading not 5 wt%. Generally, in all spraying methods patterning is not possible, problems with aerosol generation, evaporation of solvent, not well-defined edges as well as low particle loading and inhomogeneity (in thickness and solid content) in films are very common. The latter issue is more dominant in thinner films. The ultrasonic spray coating addresses some of the issues (e.g. more homogenous spraying, unclogging the nozzle) yet does not remove the disadvantage of the spraying totally. A sketch is shown in Figure 7.7. [78][10][76].

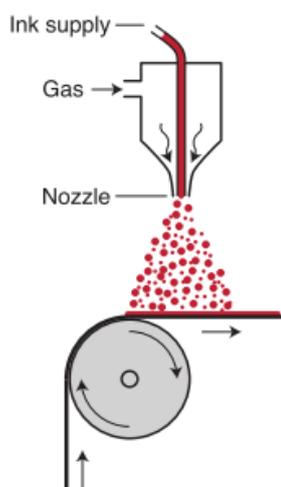


Figure 7.7. Spray coating [78]

7.5. SLOT DIE COATING

7.5.1. OVERVIEW OF SLOT DIE COATING TECHNOLOGY

The primary purpose of a slot die coating is to deposit the coating with a defined and homogeneous thickness and smoothness. The ink flows into a manifold leading the ink to the die and ultimately to the slot, thus allowing deposition onto the substrate Figure 7.8. There are two basic designs of the manifold: 1) volumetrically reducing cross section and 2) constant cross section. The design of the coat-hanger manifold can be made to fit specific applications and yet fulfill the primary criterion of even flow distribution. For proper designing a coat-hanger die, few parameters

should be taken to considerations: ink rheology, flow rate and density, processing temperature, type of solvent, heat degradation and time-dependent behavior [83].

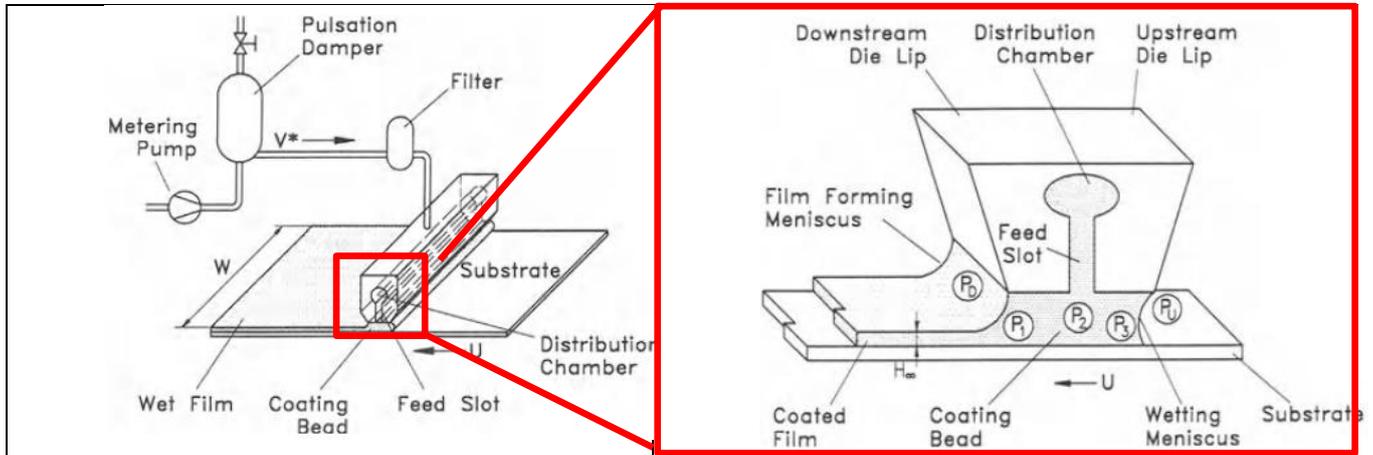


Figure 7.8. Slot Die coating scheme and part magnification [79]

As the terms Slot Die coating suggests, the ink is forced through a coating die on to the substrate with help of a pump. The average wet film thickness d is predetermined for a given feed flow rate f , coating width in the cross-web direction, w , and substrate speed, v , and is independent of rheological properties of the coating liquid, as shown in Figure 7.8 [79].

$$d = \frac{f}{v \cdot w} \cdot \frac{c}{\rho} \quad (8)$$

f : flow rate (cm^3/min), v : coating speed, w : coating width, c : solids content (g/cm^3), ρ : density

In slot die coating, viscous and capillary forces are dominant and the technique is very versatile for coating single, separate layers on to a web. Slot die method relies mainly on the formation of a stable meniscus that on upstream and downstream of the exit. The meniscus pinned at the ends of the lips depends on static equilibrium contact points at the slot-die head, which determine the advancing and receding contact angle. The position and angle of the meniscus are important for obtaining defect-free coating and are governed by two factors: shear force and pressure drop inside the liquid going through a thin channel. The stability of the two menisci is the requisite for defect-free coating and dictates the set of parameters that form stable operation ranges Figure 7.9 [80].

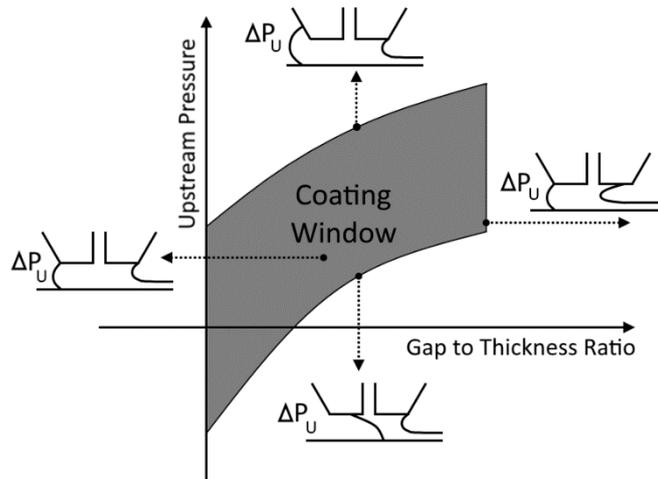


Figure 7.9. Slot die coating [80]

In slot die coating wet layer thicknesses from hundreds of nm to several μm are possible. Patterning is very limited and only possible in stripes or rectangles using masks and specially designed shim mechanisms; masks are arguably the most complex component of the system and are used to create internal patterns that convey ink streams to various slots [78][10][81].

7.5.2. TYPICAL DEFECTS IN SLOT DIE COATING

There are mainly two types of defects that can occur in slot die coating, either due to instabilities in the coating head meniscus, or to defects caused by external factors (e.g., fluid delivery, movement of the substrate, ink viscoelastic properties). The former can be corrected by modification of parameters to return to the stable coating region (Figure 7.10). To eliminate the latter, actions on the coating system or fluid delivery are often required.

The typical occurring defects are described by their characteristic features and the methods to correct them and can be listed as Chatter, Ribbing, Neck-in, Edge defects, Streaks and Bubbles (Figure 7.10) [83].

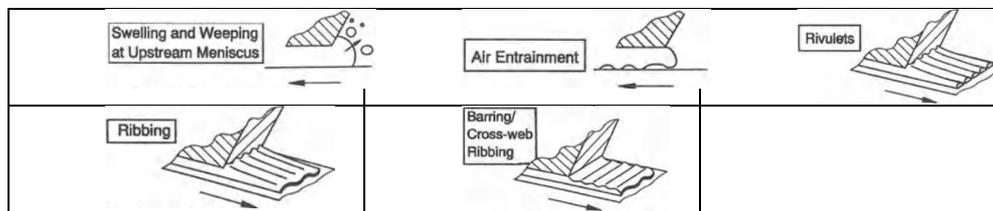


Figure 7.10. Possible defects in Slot Die coated layers [83]

7.6. MAYER ROD COATING/ BAR COATING

Mayer bar, coating rods, applicator rod, wire-wound rod, equalizer bars, rolled bars, and doctor rods are all referring to one technique, one of the oldest coating techniques known. The defining feature of the Mayer rod coater is a pool of liquid on the web that is doctored off by a rotating rod. The prototypical Mayer rod is a wire-wound rod as shown in Figure 7.11 [82].

The method is somewhat primitive and getting good control of the thickness and surface roughness. It is time and resource consuming. This method has small potential for roll-to-roll systems, especially when fast drying inks or inks with tendency to agglomeration are employed.

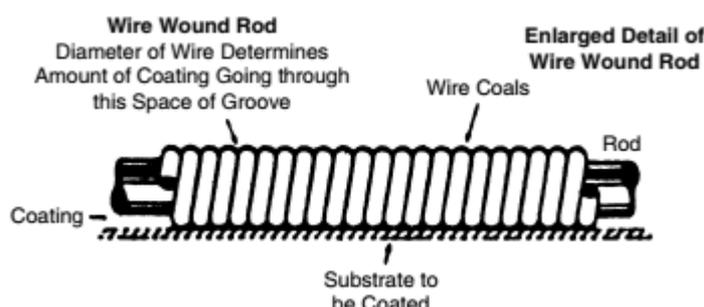


Figure 7.11. Scheme of Mayer rod [82]

8. COMPARISON OF THE PARAMETERS

Table 8.1. Comparison between different deposition methods [76][84][83][59]

| Coating method | Typical Thickness Capability | Viscosity | Particle Loading | Manufacturing speed | Roll-to-Roll capability |
|-----------------------------------|---|--------------------------------|-------------------------|----------------------------|---------------------------------------|
| Spin coating | 1-3 μm [76] | 0.01-1 Pa·s [76] | 1-20 Vol % [76] | | No |
| Doctor blade/ Tape Casting | 10 μm – 1 mm [76] | 100-130 mPa·s [76] | 10-40 Vol % [76] | 0.3 m/s [76] | Yes |
| Dip Coating | 1-50 μm [76] | < 0.01 Pa·s [76] | 0.5-5 Vol% [76] | | No |
| Spray Coating | 1-100 μm [76] | < 5×10^{-3} Pa·s [76] | < 5 Vol% [76] | | Yes |
| Rotary Screen Printing | 10-30 μm single layer (up to 100 μm multi-layer) [76][84] | 1-10 Pa·s (0.5-50 Pa·s) [84] | 10-40 vol% [76] | 2-3 m/s [84] | Yes (only for rotary screen Printing) |
| Slot Die Coating | 0.2-200 μm [83] | 0.1-30,000 Pa·s [83] | ~ 30 wt% [83] | <10 m/s [83] | Yes |
| Gravure Printing | 0.1-12 μm [84] | 0.01-0.2 Pa·s [84] | ~ 60 wt% [83] | 10-16 m/s [84] | Yes |
| InkJet | 0.01-5 μm single layer (20 μm) [84] | 0.001-0.03 Pa·s [84] | 30-60 wt% [83] | 1-5 m/s [59][84] | yes |



9. SUMMARY AND CONCLUSION

As a general guidance, ink properties are a limiting factor that impacts substantially on the choice of the most suitable method for MEA mass production. Typical inks for fuel-cell applications contain globular carbon particles loaded with catalytic nanoparticles (Pt or Pt-based alloys) mixed with surfactants and ionomer molecules. The solvent of such ink can be aqueous, yet combinations of water-isopropanol or water-ethanol are very common. The rheological behavior of those inks may vary dramatically upon preparation steps and solid content.

Spin coating is a very good method for lab-scale production but its applicability to mass production is challenged by the small area that can be coated and the difficulties in automation. Moreover, ink shear-thinning properties may cause thickness irregularities and defects at the edges of the sample. In spin coating, 95% of the solid content would be simply removed from surface during spin-off, which usually goes directly to waste. Spray coating is also another method highly used in lab production, but may not guarantee film thickness uniformity and even distribution of the particles on the substrate. In addition, nozzle clogging, uncontrolled droplet size and low particle loading act as potential weaknesses of this method. Dip coating requires very slow moving of substrate in dispersions with low solid content. Alone this factor is a strong argument against the use of dip coating in mass production. In addition, large amount of solvents is required. Mayer bar coating usually leads to high roughness and defects in coating, together with relatively poor film uniformity although roll-to-roll capabilities hold for it.

Comparing all coating and printing techniques by considering typical ink properties makes slot die coating, gravure, inkjet and screen printing as the most suitable candidates. However, screen printing (also including rotary screen printing) appears less preferable, since the carbon vulkan particles tend to clog the screen (mid- to long-term time scales), thus increasing the film defects and inhomogeneity, and exposing the process to potential machinery down time and augmenting the coating production costs.

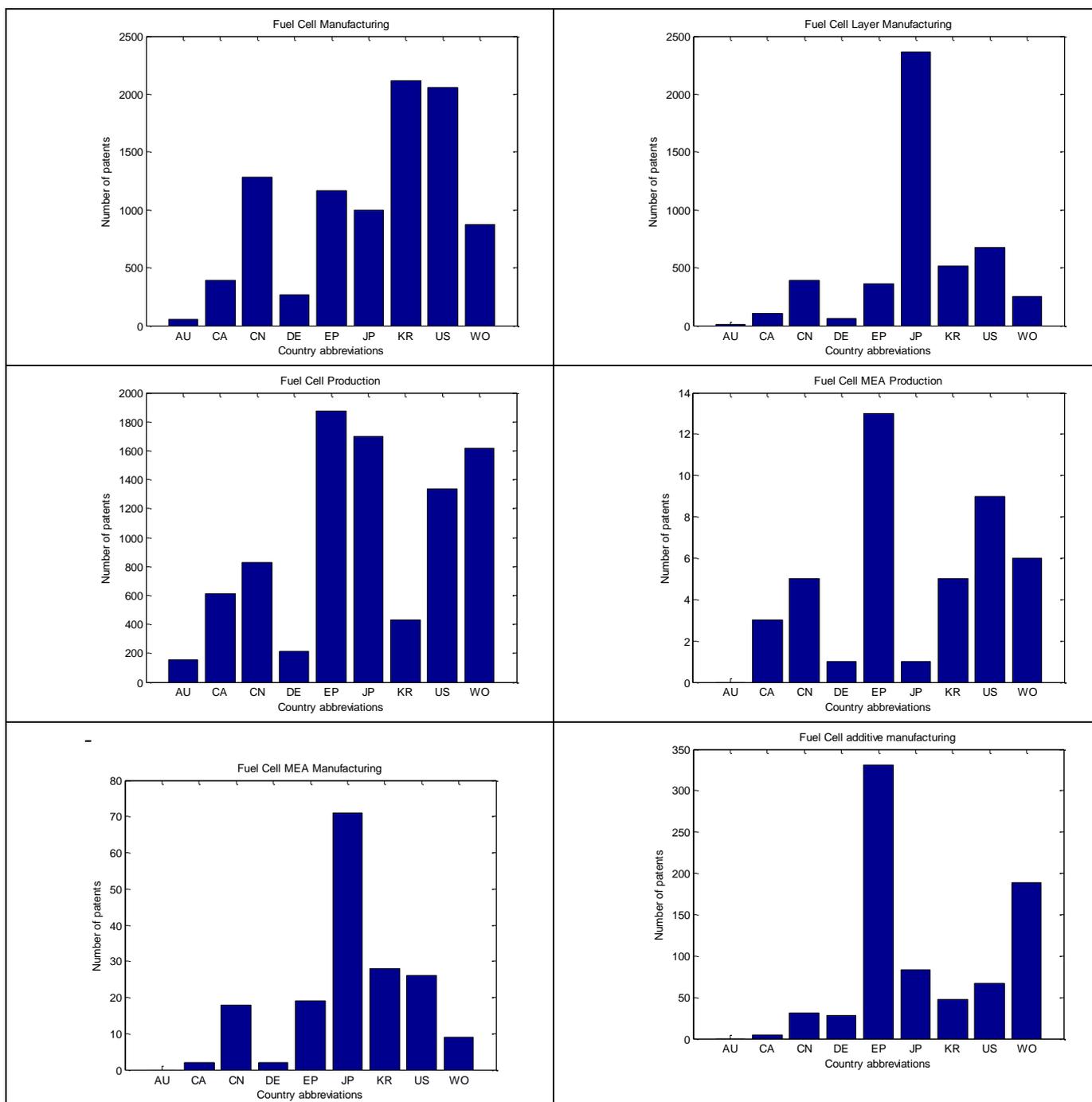
The industry partners and scientific research groups involved in this project have already extensive experience with the ultimately suggested methods. Slot die coating and screen printing are the state-of-the-art production techniques at Johnson Matthey Fuel Cell division. TU Chemnitz Digital Printing Division has extensive know-how in gravure printing and its results and methodologies have been published with relation to fuel-cell MEA production. System SPA features a rather unique experience and skill set in the use of inkjet printing, especially applied to ceramic tile manufacturing [83][85].



10. PATENTS AND ANALYSIS OF THE RESULTS

Patent search was carried out in order to establish the state-of-art in production technology for PEM fuel cells. For this purpose, a survey of different patent search engines was carried out. Patent search engines have few things in common but differ in details e.g. google offers the possibility to download the whole patent as one pdf file. But, it is very often only available in original language. On the other hand, German patent office delivers better statistics and machine translation.

Table 10.1.: Patent search from German patent office online database with general terms





Therefore, the results from the latter search engine fit better for visualization of the state of the patents and can provide better overview. This is mainly due to the ability to extract more details from the data using a search mask which provides some degree of automation in search. The patent search was based on pre-defined keywords and can be divided into two categories, first the search with general terms about fuel-cell production and second; the search with names of specific process or production methods. A small handy-tool program was written in MatLab® in order to generate diagrams from the search results by ALF¹. The resulting diagrams of searches with general key words and specific processes are presented in the table 10.1 and 10.2 accordingly. This represent the number of patents registered in various offices² therefore providing an overview which methods and applications were in the focus of research and industry plan in respective countries. WO and EP represent world intellectual property organization WIPO (www.wipo.int) and European Patent office (www.epo.org) respectively. The statistics from these shows the number of patents which were registered **in addition to** respective national offices and therefore represent the patents that have the potential to be applied in industry in global scale.

The search was carried out as part of deliverable D1.2 in the few last months and constantly updated so that the final presented results show the state-of-art in late July 2018. It is also important to note that in patent search keywords that have similar meaning might produce different statistics. For example: manufacturing and production literally refer to same meaning yet the statistics of the two search keywords are not the same. This is mainly due to language differences and preferred usage of professional vernacular.

From the table 10.2 and taken to consideration the relations, one could deduct that gravure printing and screen printing have been registered mainly in Europe. Therefore, in the focus of industry for actual or future potential methods for producing fuel cell components in this continent. On the other hand, although most registered patents about slot die coating in fuel-cell application is originated in Europe, a worldwide industry relevance is anticipated and therefore nearly all patents are also registered in WIPO in parallel. For above mentioned methods, Europe is a pioneer and other major industry nations (like USA, China as well as Korea and Japan) are lacking in number of registered patents with a substantial gap. In absolute values, the screen printing method is the champion (Figure 10.2. and Figure 10.4.) and contribution of nations like US, Japan and China is also considerable.

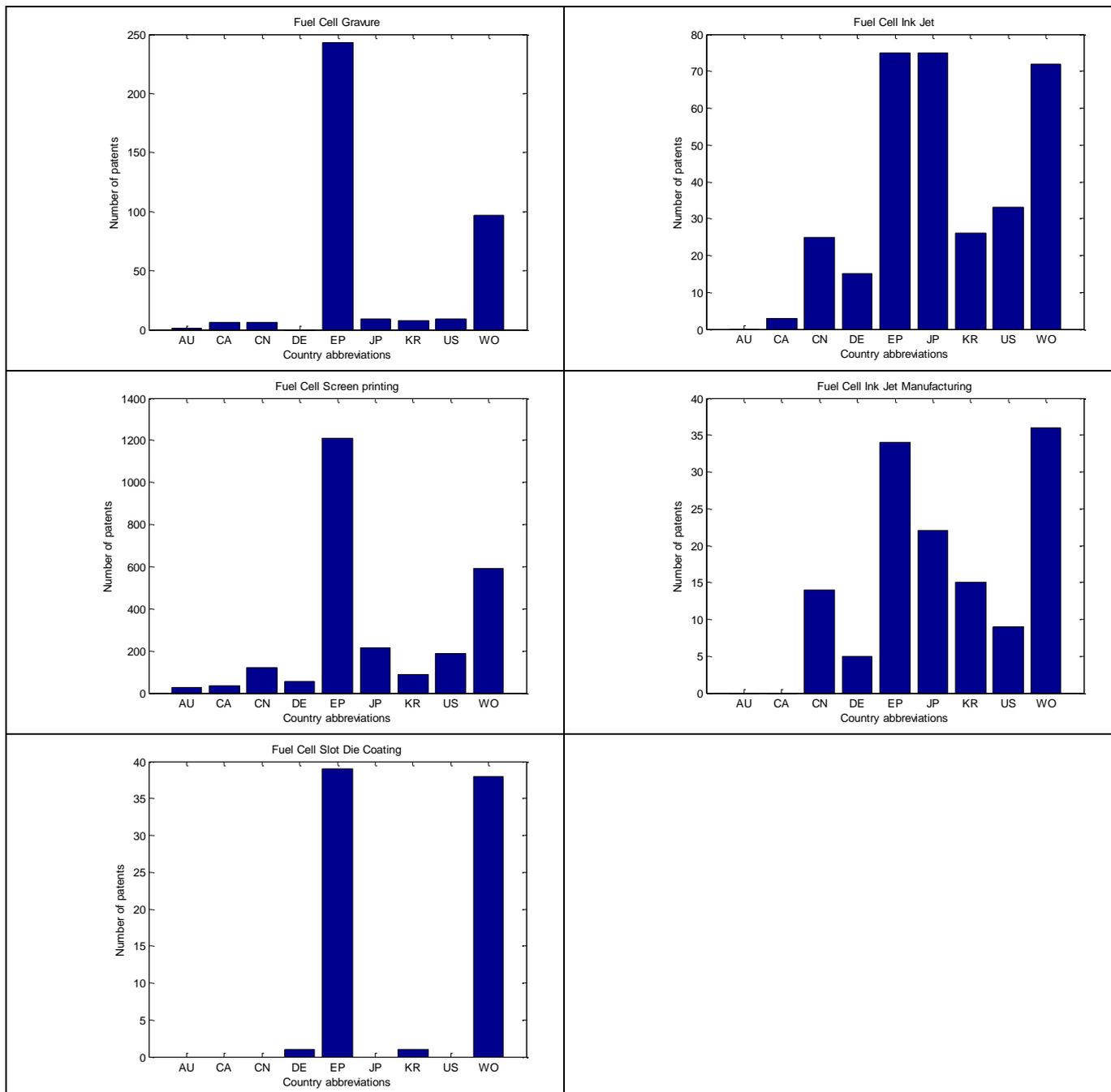
For the inkjet printing of MEA, the statistics narrate a different story. The potential of this method in production is recognized by most of the inventors and therefore many innovations are registered as patent both in national and international offices. The number of patents registered in Japan alone is nearly the same as the ones registered in Europe and in WIPO. Also other Far East industry nations like China and Korea show extended interest and innovation in this field. Yet perhaps the most important statistics from this data belongs to the number of registered patents in United States (table 10.2.), an industry nation which is heavily dependent on autos. Taking to considerations that one of the flagship electric autos (Tesla) is US-made, one can interpret these statistics as an increasing interest in local production of fuel-cell and dimming dependency to import Far East-produced Hi-energy Li-ion accumulators in mid to long terms time span.

¹ Courtesy of M.SC. Vladimir Buday

² AU: Australia, CA: Canada, CN: China, DE: Germany, EP: European Patent Office, JP: Japan, KR: Korea, US: United States of America and WO: World IP Organization WIPO



Table 10.2.: patent search from German patent office database for each specific methods





The last two diagrams offer the comparison between the productions methods registered in each patent office per each year. The search results prior to 2006 are summarized in one bar.

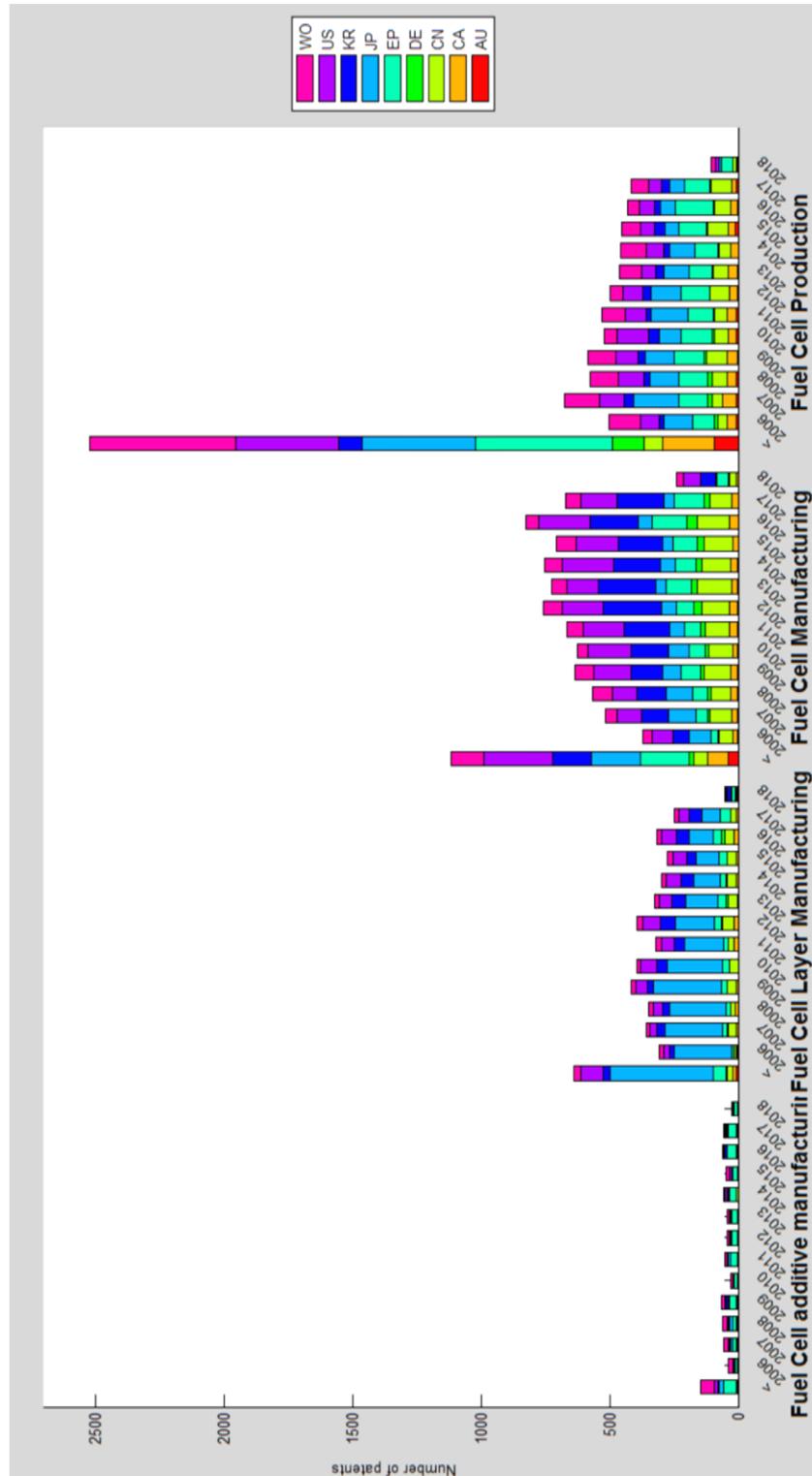


Figure 10.3.: development of number of patents for fuel cell production in the last years (various keywords: manufacturing, layer manufacturing, production, etc.)

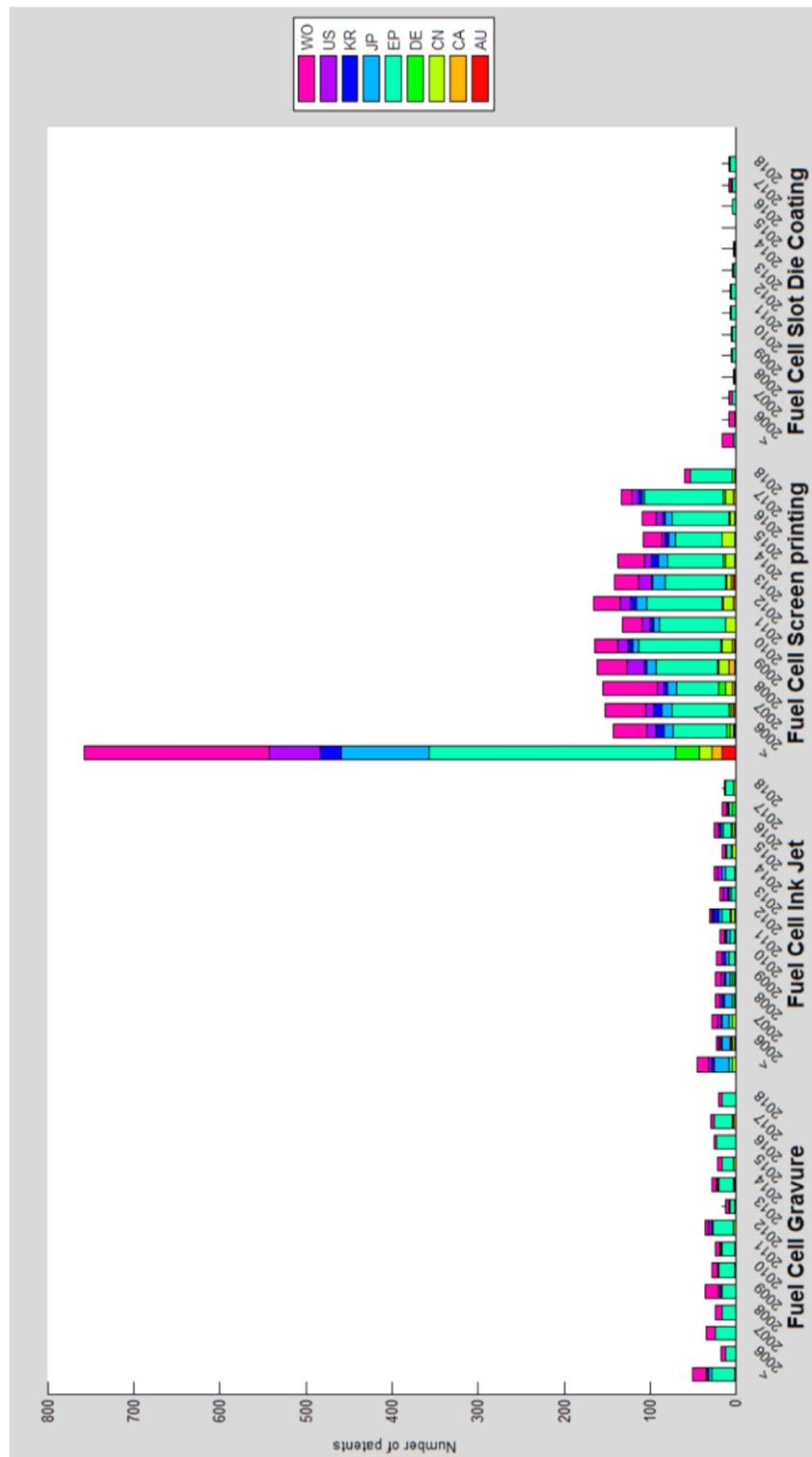


Figure 10.4.: development of number of patents for specific production methods in the last years

11. REVIEW OF THE PATENTS ABOUT THE TECHNIQUES FOR PEMFC ELECTRODES MANUFACTURING

Several patents have been collected through the following search method:

Key words: **PEMFC inkjet manufacturing** / Search engine: **Google Patent**/ Number of results: **320**

Obviously, the patent review will be a continuous activity throughout the whole duration of the project and the consortium is committed to keep itself fully and constantly updated about new patents that may arise in the field.

11.1. INKJET PRINTING OF MATERIALS FOR USE IN FUEL CELLS

Patent number: **US20090074956A1**

Priority date: 2007-09-13

ABSTRACT

A method of using **inkjet printing (IJP)** to deposit catalyst materials onto substrates such as gas diffusion layers (GDLs) that in one application are made into membrane electrode assemblies (MEAs) for polymer electrolyte fuel cells (PEMFC). The inventive IJP method can deposit smaller volumes of water-based catalyst ink solutions with picoliter precision. By optimizing the dispersion of the ink solution, this technique can be used with catalysts supported on different specimens of carbon black.

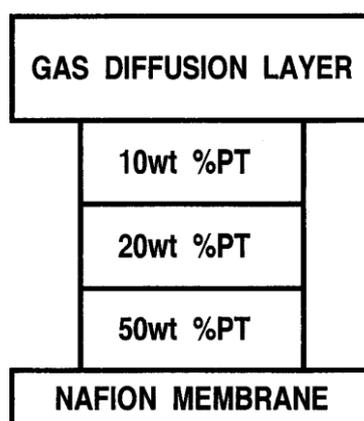


Figure 11.1. Catalyst layer graded structure

CLAIMS (14)

1. An **inkjet print apparatus** for printing an image by ejecting a material from a print head:



- a. the material including a catalyst, a metallic powder, and a polyelectrolyte in solution form, the catalyst, the metallic powder, and the polyelectrolyte being transported in a solvent.
2. The apparatus of claim 1 wherein the catalyst, the metallic powder, and the polyelectrolyte and the solvent are intermixed with each other and lie upon a substrate.
3. The apparatus of claim 2 wherein the substrate is selected from the group consisting of a gas diffusion layer, carbon paper, and a solid polyelectrolyte.
4. The apparatus of claim 3 wherein the solid polyelectrolyte comprises Nafion®.
5. The apparatus of claim 4 wherein the solid polyelectrolyte comprises Nafion® 117.
6. A method of patterning, the method comprising:
 - a. providing a substrate;
 - b. depositing a droplet including a material with a catalyst, a metallic powder, and a polyelectrolyte in solution form, the catalyst, the metallic powder, and the polyelectrolyte being transported in a solvent; and
 - c. allowing the solvent deposited on the surface of the substrate to evaporate, thereby leaving an intermixed layer of catalyst and metallic powder remaining on the substrate.
7. The method of claim 6 further comprising the step of hot pressing the material upon the substrate, thereby facilitating evaporation of the catalyst and intermixing of the catalyst and metallic powder.
8. A method of using **Inkjet printing** to deposit catalyst materials including a catalyst, a metallic powder, and a polyelectrolyte in solution form, the catalyst, the metallic powder, and the polyelectrolyte being transported in a solvent, onto gas diffusion layers for fabrication into membrane electrode assemblies deployed in polymer electrolyte fuel cells.
9. The method of claim 8 the resultant membrane electrode assembly is characterized by a Pt loading less than $0.05 \text{ mg Pt cm}^{-2}$.
10. The method of claim 8 wherein the catalyst comprises Pt and wherein the resultant membrane electrode assembly is characterized by a catalyst loading of about $0.020 \text{ mg Pt cm}^{-2}$ and Pt utilization in excess of $16,000 \text{ mgW mg}^{-1} \text{ Pt}$.
11. The method of claim 6 wherein the deposition step comprises selecting a catalyst from the group consisting of JM10, JM20, JM50 Wt % Pt on carbon black, Black Pearls 2000, M700, RC2, SC-72 and Ketjen.
12. The method of claim 6 wherein the anode catalyst layer comprises 75 Wt % of the Pt/C catalyst and 25 Wt % Nafion® solution that is dispersed with a solvent mixture.
13. The method of claim 12 further comprising the step of providing a catalyst loading of $0.021 \text{ mg Pt cm}^{-2}$ and a Pt utilization of $17,600 \text{ mWmg}^{-1} \text{ Pt}$.
14. The method of claim 13 further comprising the step of preparing a graded catalyst with a catalyst layer graded structure having a Nafion® membrane, a layer of 50 Wt % Pt, a layer of 20 Wt % Pt, a layer of 10 Wt % Pt, and a gas diffusion layer, so that the concentration of Pt decreases with distance from the Nafion® membrane.



11.2. SYSTEM AND METHOD FOR SELECTIVE DEPOSITION OF A CATALYST FOR PEM FUEL CELLS UTILIZING INKJET PRINTING

Patent number: **US20120321995A1**

Priority date: 2011-06-20

ABSTRACT

In one embodiment, a method for forming electrodes on a substrate has been developed. The method includes operating a first plurality of printheads to eject a first ink onto a first portion of the substrate and operating a second plurality of printheads to eject a second ink onto a second portion of the substrate. The first ink includes a proton transport material and an electron transport material, and the second ink includes the proton transport material, the electron transport material, and a catalyst.

CLAIMS (20)

1. A method of forming an electrode comprising:
 - a. operating a first plurality of **inkjets** to eject a first plurality of liquid drops of a first ink having a proton transport material and an electron transport material onto a first portion of a surface of a substrate; and
 - b. operating a second plurality of **inkjets** to eject a second plurality of liquid drops of a second ink having the proton transport material, the electron transport material, and a catalyst onto a second portion of the surface of the substrate, the second portion being different than the first portion.
2. The method of claim 1, wherein the proton transport material is essentially an ionomer.
3. The method of claim 2, wherein the ionomer is essentially comprised of perfluorosulfonic acid/polytetrafluoroethylene copolymer in acidic form.
4. The method of claim 1, wherein the electron transport material is essentially comprised of carbon.
5. The method of claim 1, wherein the substrate is essentially a proton exchange membrane.
6. The method of claim 5, wherein the proton exchange membrane is essentially comprised of perfluorosulfonic acid/polytetrafluoroethylene copolymer in acidic form.
7. The method of claim 1, wherein the substrate is essentially a gas diffusion layer.
8. The method of claim 7, wherein the gas diffusion layer is essentially comprised of carbon paper.
9. The method of claim 7, wherein at least a portion of the first plurality of liquid drops and the second plurality of liquid drops permeate a portion of the gas diffusion layer.
10. The method of claim 1, wherein the catalyst is essentially comprised of platinum.
11. The method of claim 1 further comprising:
 - a. operating the first plurality of **inkjets** to eject a third plurality of liquid drops of the first ink onto a first portion of another surface of the substrate; and
 - b. operating the second plurality of **inkjets** to eject a fourth plurality of liquid drops of the



- second ink onto a fourth portion of the other surface of the substrate, the fourth portion being different than the third portion.
12. The method of claim 1 further comprising:
 - a. operating the first plurality of **inkjets** to eject a third plurality of liquid drops of the first ink onto a first portion of another surface of the substrate; and
 - b. operating a third plurality of **inkjets** to eject a fourth plurality of liquid drops of a third ink having the proton transport material, the electron transport material, and another catalyst onto a fourth portion of the other surface of the substrate, the fourth portion being different than the third portion.
 13. The method of claim 12, wherein the other catalyst is essentially comprised of nickel.
 14. The method of claim 1 further comprising:
 - a. identifying an inoperable **inkjet** in the second plurality of **inkjets**;
 - b. deactivating at least a portion of the second plurality of **inkjets** in response to identifying the inoperable **inkjet**; and
 - c. activating a third plurality of **inkjet** ejectors, the third plurality of **inkjet** ejectors being configured to eject the second ink onto a same portion of the substrate as the deactivated **inkjets**.
 15. The method of claim 1 further comprising:
 - a. applying pressure to the substrate after ejecting the first plurality of liquid drops and the second plurality of liquid drops onto the surface of the substrate to spread the first plurality of liquid drops and the second plurality of liquid drops to form a single electrical conductor on the first portion and the second portion of the surface of the substrate.
 16. The method of claim 1, wherein the surface of the substrate is planar.
 17. The method of claim 16, wherein the first ink drops and the second ink drops form a planar electrical conductor on the surface of the substrate.
 18. The method of claim 17, wherein the planar electrical conductor is configured to remain electrically conductive when a pressure of between approximately 2,000 pounds per square inch (PSI) and 5,000 PSI is applied to the substrate in a fuel cell.
 19. An electrode for use in a fuel cell comprising:
 - a. a planar substrate;
 - b. a first ink formed on a first portion of a surface of the planar substrate, the first ink having a proton transport material and an electron transport material; and
 - c. a second ink formed on a second portion of the surface of the planar substrate that is different than the first portion, the second ink having the proton transport material, the electron transport material, and a catalyst, the first ink and the second ink forming a single electrical conductor over the first portion and the second portion of the surface of the substrate.
 20. The electrode of claim 19, wherein the substrate is essentially a gas diffusion layer.

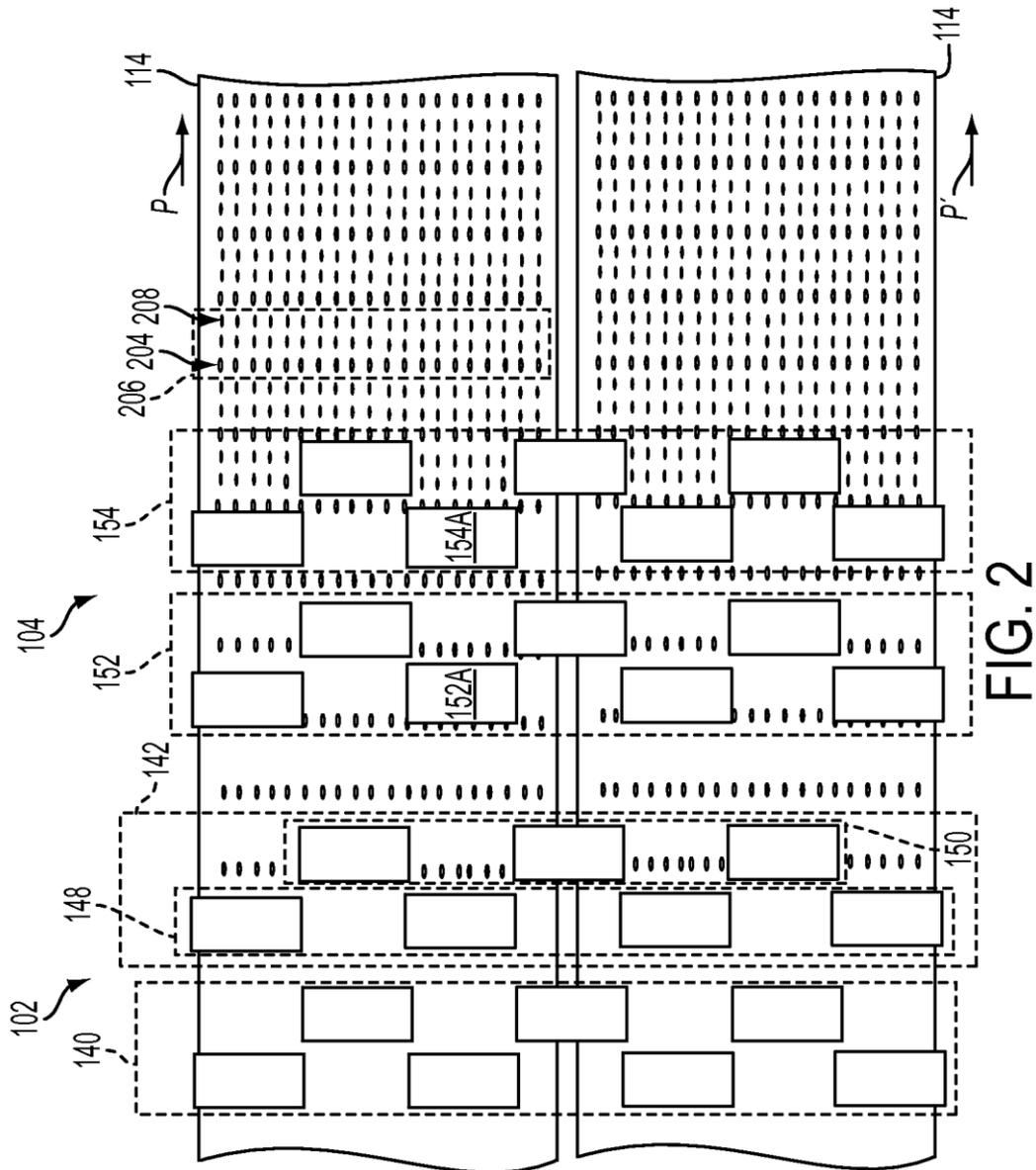


Figure 11.2.

11.3. METHODS AND APPARATUS FOR PREVENTING CLOGGING IN INK JET PRINTERS

Patent number: **US5329293A**

Priority date: 1991-04-15

ABSTRACT

Methods and apparatus are provided for preventing ink clogging in impulse ink jet printers. In preferred embodiments, the ink jet printers include at least one nozzle for ejecting ink droplets in response to a sequence of control signals and a control means unit for generating and applying the sequence to the nozzle and for controlling the amplitude of the control signals. In preferred



methods, the control unit generates a plurality of mutually asynchronous firing signals on demand, the firing signals having amplitudes which are effective to eject droplets of ink from the nozzle. The control unit also generates a plurality of mutually synchronous sub-firing signals after a predetermined interval following the firing signals, the sub-firing signals having amplitudes which are effective to prevent clogging of the nozzle yet which are ineffective to eject droplets of ink therefrom.

CLAIMS (27)

What is claimed is:

1. An impulse ink jet printer which comprises:
at least one nozzle for ejecting ink droplets in response to a sequence of control signals having controlled amplitude, said sequence comprising firing signals and sub-firing signals;
control means for generating the sequence of control signals and for controlling the amplitude of the control signals, wherein:
the control means generates a plurality of mutually asynchronous firing signals on demand, said firing signals having amplitudes which are effective to eject droplets of ink from said nozzle; and
the control means generates a plurality of mutually synchronous sub-firing signals after a predetermined quiescent interval following a sequence of said firing signals, said sub-firing signals having amplitudes which are effective to prevent clogging of the nozzle yet which are ineffective to eject droplets of ink therefrom and said generation of sub-firing signals terminating upon generation of a subsequent firing signal.
2. The printer of claim 1 wherein at least one firing signal has an amplitude of from about 50 to about 100 volts.
3. The printer of claim 1 wherein the amplitude of at least one sub-firing signal is from about 6 to about 50 percent of the amplitude of at least one firing signal.
4. The printer of claim 1 wherein the amplitude of at least one sub-firing signal is from about 12 to about 30 percent of the amplitude of at least one firing signal.
5. The printer of claim 1 wherein at least one sub-firing signal has an amplitude of from about 20 to about 50 volts.
6. The printer of claim 1 wherein at least one sub-firing signal has an amplitude of from about 24 to about 40 volts.
7. The printer of claim 1 wherein at least two sub-firing signals are generated at a frequency between about 200 and about 1000 Hz.
8. The printer of claim 1 wherein at least two sub-firing signals are generated at a frequency of about 250 Hz.
9. The printer of claim 1 wherein the control signals have controlled width and the control means controls said width.
10. The printer of claim 9 wherein at least one firing signal has a width of from about 1 to about 2 microseconds.
11. The printer of claim 9 wherein the width of at least one sub-firing signal is from about 5 to about



- 50 percent of the width of at least one firing signal.
12. The printer of claim 9 wherein the width of at least one sub-firing signal is from about 10 to about 40 percent of the width of at least one firing signal.
 13. The printer of claim 1 wherein the control signals are in digital form.
 14. An ink jet printer which comprises:
at least one nozzle for ejecting ink droplets in response to a sequence of control signals having controlled amplitude, said sequence comprising firing signals and sub-firing signals; and control means for generating the sequence of control signals and for controlling the amplitude of the control signals, wherein: the control signals are mutually asynchronous and are generated with a frequency which is effective to prevent clogging; the firing signals have amplitudes which are effective to both prevent clogging of the nozzle and to eject ink droplets; the sub-firing signals have amplitudes which are effective to prevent clogging of the nozzle yet which are ineffective to eject ink droplets; and generation of the sub-firing signals commences after a predetermined quiescent interval following generation of a firing signal and terminates upon generation of a subsequent firing signal.
 15. The impulse ink jet printer of claim 2 wherein said predetermined parameter is a predetermined amplitude.
 16. An impulse ink jet printer which comprises: at least one nozzle for ejecting ink droplets in response to a sequence of control signals having controlled amplitude, said sequence comprising firing signals and sub-firing signals; and means for controlling the amplitude of the control signals comprising: means for generating firing signals having amplitudes which are effective to eject ink droplets; means for determining elapsed time following generation of a first firing signal; and means for generating a plurality of sub-firing signals after a predetermined quiescent interval following generation of the first firing signal and for terminating said generation of sub-firing signals upon generation of a subsequent firing signal, said sub-firing signals having amplitudes which are effective to prevent clogging of the nozzle yet which are ineffective to eject ink droplets.
 17. A method of operating an impulse ink jet printer having at least one nozzle, comprising the steps of: generating a plurality of mutually asynchronous firing signals on demand, said firing signals having amplitudes which are effective to eject droplets of ink from said nozzle; and generating a plurality of mutually synchronous sub-firing signals after a predetermined quiescent interval following said firing signals, said sub-firing signals having amplitudes which are effective to prevent clogging of the nozzle yet which are ineffective to eject droplets of ink and terminating upon generation of a subsequent firing signal.
 18. A method of operating an ink jet printer which comprises at least one nozzle for ejecting ink droplets in response to a sequence of control signals comprising firing signals and sub-firing signals of controlled amplitude, said method comprising the steps of: generating a first firing signal which is effective to eject ink droplets; determining elapsed time following the generation of the first firing signal; generating a plurality of sub-firing signals after a predetermined quiescent interval following generation of the first firing signal, said sub-firing signals having a



- parameter which is effective to prevent clogging of the nozzle yet which is ineffective to eject ink droplets; and terminating said generation of sub-firing signals upon generation of a subsequent firing signal.
19. A method of operating an ink jet printer having at least one nozzle or ejecting ink droplets in response to a sequence of control signals that comprises firing signals and sub-firing signals of controlled amplitude, said method generating a sequence of control signals at a frequency which is effective to prevent clogging of the nozzle; generating firing signals having amplitudes which are effective to prevent clogging of the nozzle and to eject ink droplets; and generating sub-firing signals having amplitudes which are effective to prevent clogging of the nozzle yet which are ineffective to eject ink droplets, said generation of sub-firing signals commencing after a predetermined quiescent interval following generation of a sequence of firing signals and terminating upon generation of a subsequent firing signal.
 20. The method of claim 18 wherein the parameter is amplitude.
 21. The printer of claim 1 wherein said quiescent interval exceeds a minimum interval defined by firing signals in said sequence of firing signals.
 22. The printer of claim 1 wherein said quiescent interval is about 1 to about 360 seconds.
 23. The method of claim 1 wherein said quiescent interval exceeds a minimum interval defined by firing signals in said sequence of firing signals.
 24. The printer of claim 1 wherein said quiescent interval is about 1 to about 360 seconds.
 25. An impulse ink jet printer which comprises: at least one nozzle for ejecting ink droplets in response to a sequence of control signals having controlled amplitude, said sequence comprising firing signals and sub-firing signals; control means for generating the sequence of control signals and for controlling the amplitude of the control signals, wherein: the control means generates a plurality of mutually asynchronous firing signals on demand at varying intervals, said firing signals having amplitudes which are effective to eject droplets of ink from said nozzle; and the control means generates a plurality of mutually synchronous sub-firing signals after a predetermined quiescent interval following a sequence of said firing signals, said sub-firing signals having amplitudes which are effective to prevent clogging of the nozzle yet which are ineffective to eject droplets of ink therefrom, said quiescent interval exceeding a minimum of said varying intervals between said firing signals, and said generation of sub-firing signals terminating upon generation of a subsequent firing signal.
 26. An impulse ink jet printer which comprises: at least one nozzle for ejecting ink droplets in response to a sequence of control signals having controlled amplitude, said sequence comprising firing signals and sub-firing signals; and means for controlling the amplitude of the control signals comprising: means for generating mutually asynchronous firing signals at varying intervals, said firing signals having amplitudes which are effective to eject ink droplets; means for determining duration of said varying intervals between said firing signals; and means for generating a plurality of sub-firing signals after an interval of predetermined duration greater than a minimum of said varying intervals, said sub-firing signals having amplitudes which are effective to prevent clogging of the nozzle yet which are ineffective to eject ink droplets and said generation of sub-firing



signals terminating upon generation of a subsequent firing signal.

27. A method of operating an ink jet printer having at least one nozzle for ejecting ink droplets in response to a sequence of control signals that comprises firing signals and sub-firing signals of controlled amplitude, said method comprising the steps of:
- generating a sequence of control signals at a frequency which is effective to prevent clogging of the nozzle;
 - generating firing signals that are mutually asynchronous with varying intervals therebetween and that have amplitudes which are effective to prevent clogging of the nozzle and to eject ink droplets;
 - generating sub-firing signals that are mutually synchronous and that have amplitudes which are effective to prevent clogging of the nozzle yet which are ineffective to eject ink droplets, said generation of sub-firing signals commencing after a predetermined quiescent interval that is greater than a minimum of the varying intervals between said firing signals and terminating upon generation of a subsequent firing signal.



11.4. LAMINAR STRUCTURE AND A PRODUCTION METHOD FOR SAME

Patent number: **WO2012169836A3, US9508995B2**

Priority date: 2011-06-09

ABSTRACT

The present invention relates to a laminar structure which is used in a microporous layer, an electrode layer or the like of a membrane electrode assembly for a fuel cell, and also relates to a production method for same. The laminar structure is a laminar structure which is comprised in the membrane electrode assembly (MEA) of a polymer electrolyte membrane fuel cell (PEMFC), and comprises an electrospayed layer which is formed by the **lamination of electrospaying ink**, that has been charged by means of an electric field, through an electrospaying process in which the electrospaying ink is dispersed and **sprayed** as electrospaying liquid droplets, and, in the electrospaying process, the electrospaying substance transmission mode is set in accordance with the adjustment of electrospaying process variables. When the present invention is employed, an optimal substance transmission route is formed and three dimensional structure control is allowed through the electrospaying process and/or an **inkjet** printing process, and thus it is possible to simultaneously ensure economic advantages and durability when producing a laminated structure which is used in a microporous layer, an electrode layer or the like of a membrane electrode assembly for a fuel cell.

CLAIMS (14)

The invention claimed is:

1. A laminar structure for inclusion in a membrane-electrode assembly (MEA) of a polymer electrolyte membrane fuel cell (PEMFC), comprising an electrospayed layer formed by lamination of an electrospaying ink, which is electrically charged in electric field, in an electrospaying process in which the electrospaying ink is dispersed and sprayed as electrospaying droplets, wherein the electrospaying process sets an electrospaying substance transport mode according to adjustments of electrospaying process variables, wherein the electrospayed layer is a micro-porous layer (MPL) formed on a surface of a gas diffusion layer (GDL), wherein the micro-porous layer is formed as a multi-layered structure which includes: a first layer with dot-shaped patterns; a second layer with dot-shaped patterns, which is disposed on and in contact with the first layer; and a third layer formed by droplets smaller than droplets forming the first and second layers, which is disposed on the second layer, wherein the first, second and third layers are stacked in a thickness direction of the micro-porous layer.
2. The laminar structure as set forth in claim 1, wherein the electrospaying process variables are a feed rate of feeding the electrospaying ink, and a strength of applied voltage to form the electric field.
3. The laminar structure as set forth in claim 2, wherein the electrospaying substance transport mode comprises a drop mode in which the electrospayed layer is formed to have the dot-shaped patterns, and a jetting mode in which thickness of the electrospayed layer and structure



of pores formed in the electro sprayed layer are controlled, wherein the jetting mode is set when the feed rate of feeding the electro spraying ink is greater, or when the strength of the applied voltage is greater than in the drop mode.

4. The laminar structure as set forth in claim 1, further comprising an **inkjet** layer which is formed by lamination of an **inkjet** ink in an **inkjet** printing process in which the **inkjet** ink is jetted out of an **inkjet** nozzle, wherein the ink printing process sets an **inkjet** substance transport mode according to adjustments of **inkjet** process variables.
5. The laminar structure as set forth in claim 4, wherein the **inkjet** process variables are a size of the **inkjet** nozzle, and a cycle of jetting the **inkjet** ink.
6. The laminar structure as set forth in claim 4, wherein the **inkjet** substance transport mode comprises: a dot mode deposition in which the **inkjet** ink is jetted in a form of **inkjet** droplets so that the **inkjet** layer is formed into a dot-like pattern, and a line mode deposition in which the **inkjet** ink is continuously jetted so that the **inkjet** layer is formed into a line pattern, wherein the line mode deposition is set, when a size of the **inkjet** nozzle is greater, or a cycle of jetting the **inkjet** is shorter than in the dot mode deposition.
7. The laminar structure as set forth in claim 1, wherein one or more electro sprayed layers are formed, and the one or more electro sprayed layers are continuously formed by a roll-to-roll manner.
8. The laminar structure as set forth in claim 4, wherein the **inkjet** layer micro-porous layer (MPL) formed on the surface of the gas diffusion layer (GDL).
9. The laminar structure as set forth in claim 8, wherein the micro-porous layer is provided as a porous graded structure based on adjustments of one or more of the electro spraying substance transport mode and the **inkjet** substance transport mode.
10. The laminar structure as set forth in claim 4, wherein one or more electro sprayed layers are formed, one or more **inkjet** layers are formed, and the one or more electro sprayed layers and the one or more **inkjet** layers are continuously formed by a roll-to-roll manner.
11. A laminar structure for inclusion in a membrane-electrode assembly (MEA) of a polymer electrolyte membrane fuel cell (PEMFC), comprising an electro sprayed layer formed by lamination of an electro spraying ink, which is electrically charged in electric field, in an electro spraying process in which the electro spraying ink is dispersed and sprayed as electro spraying droplets, wherein the electro spraying process sets an electro spraying substance transport mode according to adjustments of electro spraying process variables, wherein the electro sprayed layer is a micro-porous layer (MPL) formed on a surface of a gas diffusion layer (GDL), wherein the micro-porous layer is formed as a multi-layered structure which includes: a first layer with dot-shaped patterns; a second layer formed by droplets smaller than droplets forming the first layer, which is disposed on and in contact with the first layer; and a third layer with dot-shaped patterns, which is disposed on and in contact with the second layer, the third layer being formed by droplets larger than the droplets forming the second layer, wherein the first, second and third layers are stacked in a thickness direction of the micro-porous layer.
12. The laminar structure as set forth in claim 11, wherein the micro-porous layer further includes a



fourth layer formed by droplets smaller than the droplets forming the first and third layers, which is disposed on and in contact with the third layer, wherein the first, second, third and fourth layers are stacked in the thickness direction of the micro-porous layer.

13. A laminar structure for inclusion in a membrane-electrode assembly (MEA) of a polymer electrolyte membrane fuel cell (PEMFC), comprising an electrospayed layer formed by lamination of an electrospaying ink, which is electrically charged in electric field, in an electrospaying process in which the electrospaying ink is dispersed and sprayed as electrospaying droplets, wherein the electrospaying process sets an electrospaying substance transport mode according to adjustments of electrospaying process variables, wherein the electrospayed layer is a catalytic electrode layer of a laminated structure made of multiple layers, which include: a first layer formed of a first catalyst material in which a first adjusted content of platinum (Pt) is contained; and a second layer formed on the first layer, the second layer being formed of a second catalyst material in which a second adjusted content of platinum (Pt) is contained, wherein the first and second layers are stacked in a thickness direction of the catalytic electrode layer.
14. A laminar structure for inclusion in a membrane-electrode assembly (MEA) of a polymer electrolyte membrane fuel cell (PEMFC), comprising an electrospayed layer formed by lamination of an electrospaying ink, which is electrically charged in electric field, in an electrospaying process in which the electrospaying ink is dispersed and sprayed as electrospaying droplets, wherein the electrospaying process sets an electrospaying substance transport mode according to adjustments of electrospaying process variables, wherein the electrospayed layer is a catalytic electrode layer of a laminated structure made of multiple layers, each of the multiple layers being formed of a catalyst material in which a constant platinum (Pt) content is contained, wherein the multiple layers include: a first layer formed of a first adjusted weight ratio of the catalyst material; and a second layer formed of a second adjusted weight ratio of the catalyst material, wherein the first and second layers are stacked in a thickness direction of the catalytic electrode layer.

Fig. 6

Roll-to-roll base coat-on-demand platform
for MEA fabrication

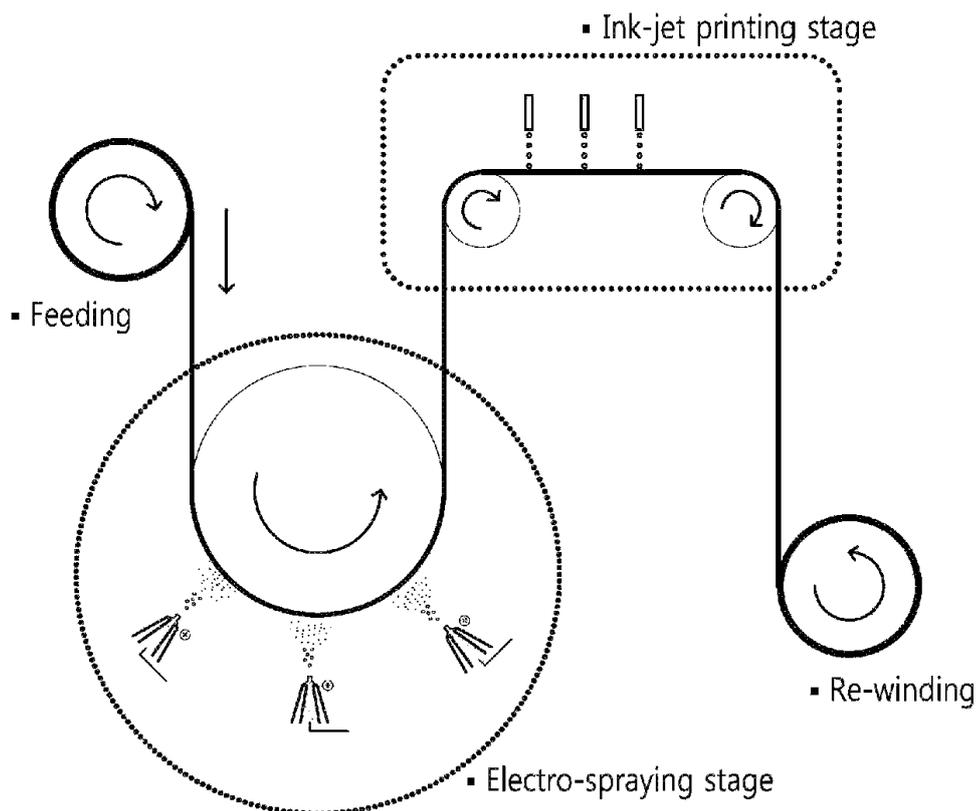


Figure 11.3. Conceptual view of a manufacturing method of a laminar structure according to roll-to-roll manner.



11.5. ELECTROCATALYST INKS FOR FUEL CELL APPLICATIONS

Patent number: **US7696122B2**

Priority date: 2006-07-05

ABSTRACT

An electrocatalyst ink composition comprising a liquid vehicle, particles comprising at least one electrocatalyst metal, and at least one copolymer dispersant comprising at least one polyalkylene oxide segment.

CLAIMS (22)

1. An electrocatalyst ink composition comprising a liquid vehicle, 10 to 60 wt % of the ink composition of particles comprising at least one electrocatalyst metal, and at least one polyoxyalkyleneamine comb-branched copolymer dispersant.
2. The ink composition of claim 1, wherein the liquid vehicle comprises at least 50% wt of water.
3. The ink composition of claim 1, wherein said at least one electrocatalyst metal is selected from platinum, silver, palladium, ruthenium, osmium and alloys thereof.
4. The ink composition of claim 1, wherein said at least one electrocatalyst metal is supported on a particulate carrier material.
5. The ink composition of claim 4, wherein the particulate carrier material comprises carbon or a metal oxide.
6. The ink composition of claim 1, wherein said particles have an average size less than 300 nm.
7. The ink composition of claim 1, wherein said particles have a density of about 5 to about 20 gm/cc.
8. The ink composition of claim 1, wherein said at least one electrocatalyst metal comprises 10 to 20 wt % of the ink composition.
9. The ink composition of claim 1, wherein the comb-branched copolymer dispersant has a molecular weight of from about 1,000 to about 100,000.
10. The ink composition of claim 1, wherein the comb-branched copolymer dispersant has a molecular weight of from about 5,000 to about 80,000.
11. The ink composition of claim 1, wherein the comb-branched copolymer dispersant has a molecular weight of from about 10,000 to about 50,000.
12. The ink composition of claim 1, wherein said polyoxyalkyleneamine comprises primary amino groups attached to the terminus of a polyether backbone.
13. The ink composition of claim 1, wherein the dispersant is water-soluble.
14. The ink composition of claim 1 and comprising greater than or equal to 30 parts by weight of the copolymer dispersant to 100 parts by weight of said particles comprising at least one electrocatalyst metal.



15. The ink composition of claim 1 and further comprising a proton-conducting polymer.
16. A method for the fabrication of an electrocatalyst layer, comprising the steps of: a) depositing an ink composition onto a substrate, said ink composition comprising a liquid vehicle, 10 to 60 wt % of particles comprising at least one electrocatalyst metal, and at least one polyoxyalkyleneamine comb-branched copolymer dispersant.
17. The method of claim 16, wherein said depositing step comprises depositing said ink composition using a direct-write tool.
18. The method of claim 17, wherein said direct-write tool is an ink-jet device.
19. The method of claim 16 and further comprising the step of washing the substrate after deposition of the ink composition to remove the dispersant.
20. The method of claim 16, wherein said substrate is an ion exchange membrane.
21. A catalyst coated membrane prepared by the method of claim 20.
22. A fuel cell comprising a catalyst coated membrane of claim 21.



11.6. PEMFC ELECTRODE STRUCTURING

Patent number: **US20140127605A1**

Priority date: 2012-11-08

ABSTRACT

A method of deposition, by drop-on-demand **inkjet printing**, of the catalytic layer of a fuel cell comprising the deposition, on a printing surface, of an ink generating substantially circular structures comprising a bead at their periphery.

CLAIMS (14)

1. A method of deposition, by drop-on-demand (DOD) **inkjet printing**, of a catalytic layer of a fuel cell comprising depositing, on a printing surface, an ink generating substantially circular structures comprising a bead at their periphery.
2. The deposition method of claim 1, wherein the printing surface is an electrolytic membrane or a gas diffusion layer of the fuel cell.
3. The method of claim 1, wherein it comprises the steps of:
 - a. expelling ink drops through a printing nozzle, advantageously having an opening with a diameter in the range between 10 and 100 micrometers, towards the printing surface;
 - b. drying the deposited drops, advantageously at a temperature greater than or equal to 40° C.
4. The deposition method of claim 3, according to which the steps of expelling the drops towards the printing surface and of drying are iteratively repeated.
5. A catalytic layer for a fuel cell capable of being obtained by means of the method of claim 1, appearing in the form of substantially circular structures comprising a bead at their periphery and having an external diameter smaller than 1 millimeter, advantageously in the range between 20 and 200 micrometers.
6. The catalytic layer for a fuel cell of claim 5, wherein the structures have an external diameter equal to 50 micrometers.
7. The catalytic layer for a fuel cell of claim 5, wherein the width of the beads of the structures represents from 5 to 20% of the external diameter of the structures.
8. The catalytic layer for a fuel cell of claim 6, wherein the width of the heads of the structures represents from 5 to 20% of the external diameter of the structures.
9. The catalytic layer for a fuel cell of claim 5, wherein the structures are spaced apart from one another by a distance greater than or equal to 10 micrometers.
10. An electrolytic membrane for a fuel cell having on at least one of its surfaces, structures such as defined in claim 5.
11. A gas diffusion layer for a fuel cell having on at least one of its surfaces, structures such as defined in claim 5.
12. A fuel cell comprising the catalytic layer of claim 5.
13. A fuel cell comprising the electrolytic membrane of claim 9.
14. A fuel cell comprising at least one gas diffusion layer of claim 10.



11.7. FUEL CELL AND PRODUCTION METHOD THEREOF

Patent number: **US20050142433A1**

Priority date 2003-12-25

ABSTRACT

In order to prevent the crossover of an organic fuel such as methanol in a fuel cell and to exhibit excellent electricity generation characteristics without impairing the utilization efficiency of the fuel, at least either of (1) a discontinuous catalyst layer being formed on a surface of an anode catalyst layer and having a higher density (existence probability) of platinum type catalyst than the anode catalyst layer and (2) an electrolyte polymer layer is formed at the interface between the anode catalyst layer and a polymer electrolyte membrane.

CLAIMS (15)

1. A fuel cell for generating electricity using a fuel and an oxidant comprising:
 - a. a hydrogen ion conductive polymer electrolyte membrane;
 - b. an anode including an anode catalyst layer on one surface of said polymer electrolyte membrane, and an anode diffusion layer on the outer surface of said anode catalyst layer; and
 - c. a cathode including a cathode catalyst layer on the other surface of said polymer electrolyte membrane, and a cathode diffusion layer on the outer surface of said cathode catalyst layer,
 - d. wherein said anode catalyst layer includes conductive carbon particles supporting a platinum type catalyst thereon and a hydrogen ion conductive polymer electrolyte, and
 - e. at least either of (1) a discontinuous catalyst layer being formed on a surface of said anode catalyst layer and having a higher density of platinum type catalyst than said anode catalyst layer and (2) an electrolyte polymer layer is provided at the interface between said anode catalyst layer and said polymer electrolyte membrane.
2. The fuel cell in accordance with claim 1, wherein said discontinuous catalyst layer comprises a plurality of catalyst islands.
3. The fuel cell in accordance with claim 1, wherein the ratio (Pt/C) of platinum atoms to carbon atoms on the surface of said anode catalyst layer having said discontinuous catalyst layer is 0.2 to 0.8 at the discontinuous catalyst layer side.
4. The fuel cell in accordance with claim 1, wherein said platinum type catalyst is an alloy or mixture containing platinum and at least one selected from the group consisting of ruthenium, iron, cobalt, nickel, chromium, molybdenum, rhodium, palladium, osmium and iridium.
5. The fuel cell in accordance with claim 1, wherein said electrolyte polymer layer is made of a polymer electrolyte having at least one ion conductive functional group selected from the group consisting of a phosphonyl group, a phosphinyl group, a sulfonyl group, a sulfinyl group, a carboxyl group, a sulfone group, a mercapto group, an ether bond group, a hydroxyl group, a quaternary ammonium group, an amino group and a phosphate group.
6. The fuel cell in accordance with claim 5, wherein said electrolyte polymer layer is formed by a wet application process in which a solution containing said polymer electrolyte is applied onto said anode catalyst layer.



7. The fuel cell in accordance with claim 1, wherein said fuel contains at least one organic compound selected from the group consisting of methanol, dimethyl ether and ethylene glycol, and said fuel cell is a direct fuel type fuel cell.
8. A method for producing a fuel cell comprising the steps of:
 - a. forming a catalyst layer containing at least conductive carbon particles supporting a platinum type catalyst thereon and a hydrogen ion conductive polymer electrolyte;
 - b. forming a discontinuous catalyst layer or an electrolyte polymer layer on the surface of said catalyst layer; and
 - c. placing a hydrogen ion conductive polymer electrolyte membrane on the surface of said catalyst layer at the discontinuous catalyst layer side or the electrolyte polymer layer side and hot pressing said catalyst layer and said polymer electrolyte membrane to be integrated.
9. The method for producing a fuel cell in accordance with claim 8, wherein said discontinuous catalyst layer is formed by plasma chemical-vapor deposition using an organic metal complex containing a platinum-based metal.
10. The method for producing a fuel cell in accordance with claim 9, wherein said plasma chemical-vapor deposition is performed by applying an alternating voltage only or a direct voltage with a superimposed alternating voltage to generate glow discharge plasma.
11. The method for producing a fuel cell in accordance with claim 8, wherein said discontinuous catalyst layer is formed on the surface of said catalyst layer by spraying an ink containing at least a platinum type catalyst and an organic dispersion medium on the surface of said catalyst layer by means of an ink jet method or spraying method.
12. A method for producing a fuel cell comprising the steps of:
 - a. forming a catalyst layer containing at least conductive carbon particles supporting a platinum type catalyst thereon and a hydrogen ion conductive polymer electrolyte;
 - b. forming a discontinuous catalyst layer on the surface of said catalyst layer;
 - c. forming an electrolyte polymer layer on the surface of said catalyst layer at the discontinuous catalyst layer side by a wet application process; and
 - d. placing a hydrogen ion conductive polymer electrolyte membrane on the surface of said electrolyte polymer layer and hot pressing said catalyst layer and said polymer electrolyte membrane to be integrated.
13. The method for producing a fuel cell in accordance with claim 12, wherein said discontinuous catalyst layer is formed by plasma chemical-vapor deposition using an organic metal complex containing a platinum-based metal.
14. The method for producing a fuel cell in accordance with claim 13, wherein said plasma chemical-vapor deposition is performed by applying an alternating voltage only or a direct voltage with a superimposed alternating voltage to generate glow discharge.
15. The method for producing a fuel cell in accordance with claim 12, wherein said discontinuous catalyst layer is formed on the surface of said catalyst layer by spraying an ink containing at least a platinum type catalyst and an organic dispersion medium on the surface of said catalyst layer by means of an ink jet method or spraying method.

FIG. 3

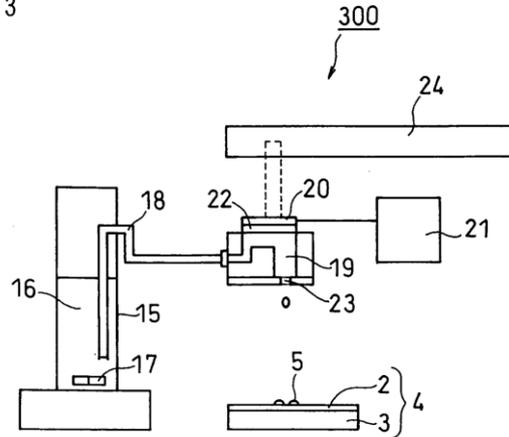


FIG. 4

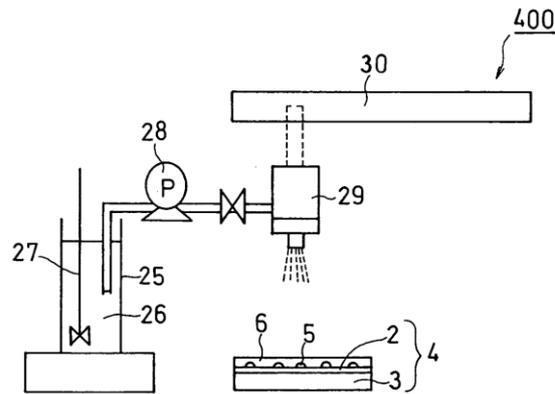


Figure 11.4. Schematic diagram illustrating the structure of a spray type application apparatus used in a method for producing a fuel cell.



11.8. FUEL CELL, METHOD OF MANUFACTURING THE SAME, ELECTRONIC APPARATUS, AND AUTOMOBILE

Patent number: **US20040191410A1**

Priority date: 2003-03-31

ABSTRACT

To provide a method to effectively manufacture a fuel cell having high output density and excellent cell characteristics, and an electronic apparatus and an automobile including the fuel cell as a power supply, the fuel cell including reaction layers with high reaction efficiency and current collecting layers to effectively collect electrons generated from the reaction layers. A method of manufacturing a fuel cell, which includes a first current collecting layer, a first reaction layer, an electrolyte membrane, a second reaction layer, and a second current collecting layer, and an electronic apparatus and an automobile, which include the fuel cell as a power supply, are provided, the manufacturing method including forming the first reaction layer by repeatedly applying a predetermined amount of reaction-layer-forming material on the first current collecting layer at predetermined intervals.

CLAIMS (8)

What is claimed is:

1. A method of manufacturing a fuel cell including a first current collecting layer, a first reaction layer, an electrolyte membrane, a second reaction layer, and a second current collecting layer, the method comprising:
 - a. forming the first reaction layer by repeatedly applying a reaction-layer-forming material on the first current-collecting layer at predetermined intervals.
2. A method of manufacturing a fuel cell, comprising:
 - a. on a first substrate, forming first gas passages to supply first reaction gas;
 - b. forming a first current collecting layer to collect electrons generated by a reaction of the first reaction gas supplied through the first gas passages;
 - c. forming a first reaction layer to cause the first reaction gas supplied through the first gas passages to react with a catalyst;
 - d. forming an electrolyte membrane;
 - e. on a second substrate, forming second gas passages to supply second reaction gas;
 - f. forming a second current collecting layer to collect electrons which are subjected to a reaction with the second reaction gas supplied through the second gas passages; and
 - g. forming a second reaction layer to cause the second reaction gas supplied through the second gas passages to react with a catalyst,
 - h. at least one of forming the first reaction layer and forming the second reaction layer forming the first reaction layer or the second reaction layer by repeatedly applying a reaction-layer-forming material on the first current collecting layer or the second current collecting layer at predetermined intervals.
3. The method of manufacturing a fuel cell according to claim 1,
 - a. a discharging device* is employed to apply the reaction-layer-forming material.
4. The method of manufacturing a fuel cell according to claim 1,



- a. the first reaction layer being formed by removing unnecessary components from a film, which is obtained by applying the reaction-layer-forming material, under reduced pressure and at a temperature no greater than 100° C.
5. The method of manufacturing a fuel cell according to claim 1,
 - a. the first reaction layer being formed by repeating a unit operation in which a given amount of the reaction-layer-forming material is applied on the entire area of a first reaction layer forming region on the first current collecting layer at predetermined intervals and unnecessary components are removed from droplets of the applied reaction-layer-forming material.
6. The method of manufacturing a fuel cell according to claim 5,
 - a. the discharging device being provided with a plurality of discharging nozzles, and the reaction-layer-forming material being discharged and applied during every unit operation by a different discharging nozzle.
7. An electronic apparatus, comprising:
 - a. a fuel cell manufactured by a method according to claim 1 as a power supply.
8. An automobile, comprising:
 - a. a fuel cell manufactured by a method according to claim 1 as a power supply.

* In the text the inkjet system is used as discharging device



11.9. CATALYST LAYER WITH THROUGH-HOLES FOR FUEL CELLS

Patent number: **US20160133944A1**

Priority date: 2014-11-07

ABSTRACT

The performance of solid polymer electrolyte fuel cell stacks can be improved by incorporating an appropriate set of through-holes in the catalyst layers, and particularly in the cathode catalyst layers. Intaglio methods suitable for manufacturing catalyst layers with through-holes are disclosed.

CLAIMS (20)

What is claimed is:

1. An intaglio method of making a catalyst coated membrane, the catalyst coated membrane comprising a solid polymer electrolyte membrane coated with a catalyst layer, the catalyst layer comprising a plurality of through-holes, the method comprising:
 - a. providing a printing surface comprising a depression and a plurality of pillars arranged in a pattern within the depression;
 - b. filling the depression with an ink comprising the catalyst;
 - c. drying the ink in the depression of the printing surface;
 - d. contacting a sheet of the solid polymer electrolyte to the printing surface; and
 - e. applying pressure and heat to the contacted solid polymer electrolyte and printing surface, thereby making the catalyst coated membrane wherein the plurality of through-holes are located in accordance with the locations of the plurality of pillars in the printing surface.
2. The intaglio method of claim 1 wherein the printing surface is a plate or a drum.
3. The intaglio method of claim 1 wherein the plurality of pillars are shaped as right circular cylinders.
4. The intaglio method of claim 1 wherein the equivalent diameter of the pillars is in the range from about 1 to 500 micrometers.
5. The intaglio method of claim 1 wherein the plurality of pillars in the pattern are spaced apart with an average spacing of from about 4 to 1000 micrometers.
6. The intaglio method of claim 1 wherein the filling comprises **inkjet printing**.
7. The intaglio method of claim 1 wherein the filling comprises overfilling the depression with the ink and squeegeeing away excess ink from the surfaces of the plurality of pillars and the printing surface surrounding the depression.
8. The intaglio method of claim 1 comprising applying pressure to the contacted solid polymer electrolyte and printing surface in the range from about 5 to 16 bar.
9. The intaglio method of claim 1 comprising applying heat to the contacted solid polymer electrolyte and printing surface in the range from about 100 to 150° C.
10. The intaglio method of claim 1 wherein the coated catalyst layer is from about 1.5 to 15 micrometers thick.
11. The intaglio method of claim 1 wherein the coated catalyst layer comprises from about 0.01 to 0.5 mg/cm² of platinum catalyst.
12. A solid polymer electrolyte fuel cell stack comprising a series stack of solid polymer electrolyte



- fuel cells wherein the solid polymer electrolyte fuel cells each comprise:
- a. a catalyst coated membrane comprising:
 - b. a solid polymer electrolyte;
 - c. an anode layer comprising anode catalyst coated on one side of the solid polymer electrolyte; and
 - d. a cathode layer comprising anode catalyst coated on the other side of the solid polymer electrolyte;
 - e. an anode gas diffusion layer adjacent the anode layer of the catalyst coated membrane;
 - f. a cathode gas diffusion layer adjacent the cathode layer of the catalyst coated membrane; and
 - g. characterized in that the cathode layer comprises a plurality of through-holes arranged in a pattern.
13. The solid polymer electrolyte fuel cell stack of claim 12 wherein the plurality of through-holes are shaped as right circular cylinders.
 14. The solid polymer electrolyte fuel cell stack of claim 12 wherein the equivalent diameter of the through-holes is in the range from about 1 to 500 micrometers.
 15. The solid polymer electrolyte fuel cell stack of claim 12 wherein the plurality of through-holes in the pattern are spaced apart with an average spacing of from about 4 to 1000 micrometers.
 16. The solid polymer electrolyte fuel cell stack of claim 12 wherein the coated catalyst layer is from about 1.5 to 15 micrometers thick.
 17. The solid polymer electrolyte fuel cell stack of claim 12 wherein the coated catalyst layer comprises from about 0.01 to 0.5 mg/cm² of platinum catalyst.
 18. The solid polymer electrolyte fuel cell stack of claim 12 wherein the plurality of through-holes occupies about 1 to 20% of the area of the cathode layer.
 19. The solid polymer electrolyte fuel cell stack of claim 12 wherein the ratio of the equivalent diameter of the through-holes to the average spacing of the through-holes is from about 0.1 to 0.5.
 20. A method of operating the solid polymer electrolyte fuel cell stack of claim 12 comprising:
 - a. supplying fuel to the anode layers in the fuel cells at greater than ambient pressure;
 - b. supplying oxidant to the cathode layers in the fuel cells at greater than ambient pressure; and
 - c. drawing power at greater than 1 W/cm² from the fuel cells.

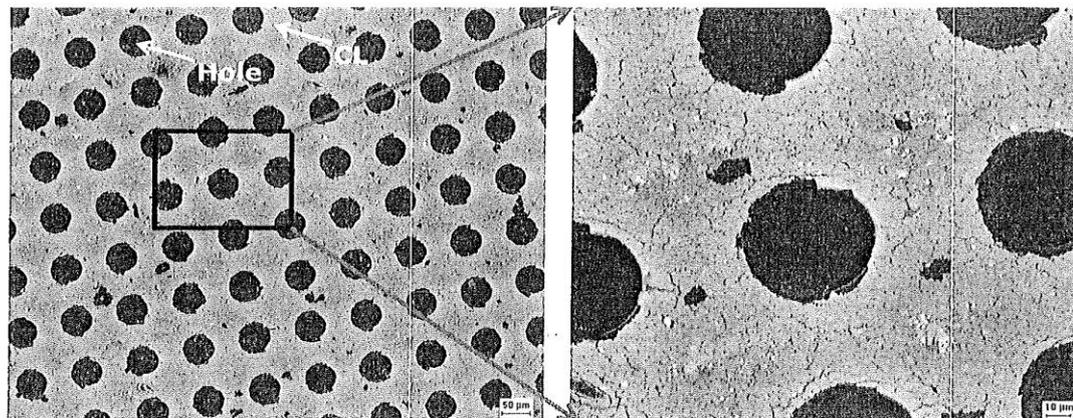


FIG. 3a

FIG. 3b

Figure 11.5. Examples in which an intaglio method was employed and inkjet printing was used for the filling step. FIG. 3b shows an enlarged view of a section in FIG. 3 a.



11.10. FUEL CELL STACK ASSEMBLY AND METHOD OF ASSEMBLY

Patent number: **WO2015101772A1**

Priority date : 2013-12-31

ABSTRACT

A method of manufacturing a membrane electrode assembly for a fuel cell comprising a proton exchange membrane and a catalyst layer including a catalyst, the method comprising; forming a gas diffusion layer comprising graphene.

In the Description part

“The gas diffusion layer and/or microporous layer may be formed by printing. This is an advantageous way of forming the layer to provide precise control of porosity, for example, and other structural properties. The printing technique may be **inkjet printing**, 3D printing or additive printing among others. “

“Figure 8 illustrates an example method of forming a catalyst layer. The method comprises receiving a proton exchange membrane at step 80. Step 81 illustrates forming a catalyst layer comprising graphene onto the proton exchange membrane. Step 81 may be achieved by printing, such as **inkjet printing** or additive printing. “

11.11. FUEL CELL STACK ASSEMBLY AND METHOD OF ASSEMBLY

Patent number: **US20160329586A1**

Priority date : 2013-12-31

ABSTRACT

A method of manufacturing a membrane electrode assembly for a fuel cell comprising a proton exchange membrane and a catalyst layer including a catalyst, the method comprising; forming a gas diffusion layer comprising graphene.

“The gas diffusion layer and/or microporous layer may be formed by printing. This is an advantageous way of forming the layer to provide precise control of porosity, for example, and other structural properties. The printing technique may be **inkjet printing**, 3D printing or additive printing among others.”

In Figure 11.6. “FIG. 8 illustrates an example method of forming a catalyst layer. The method comprises receiving a proton exchange membrane at step **80**. Step **81** illustrates forming a catalyst layer comprising graphene onto the proton exchange membrane. Step **81** may be achieved by printing, such as **inkjet printing or additive printing**.”

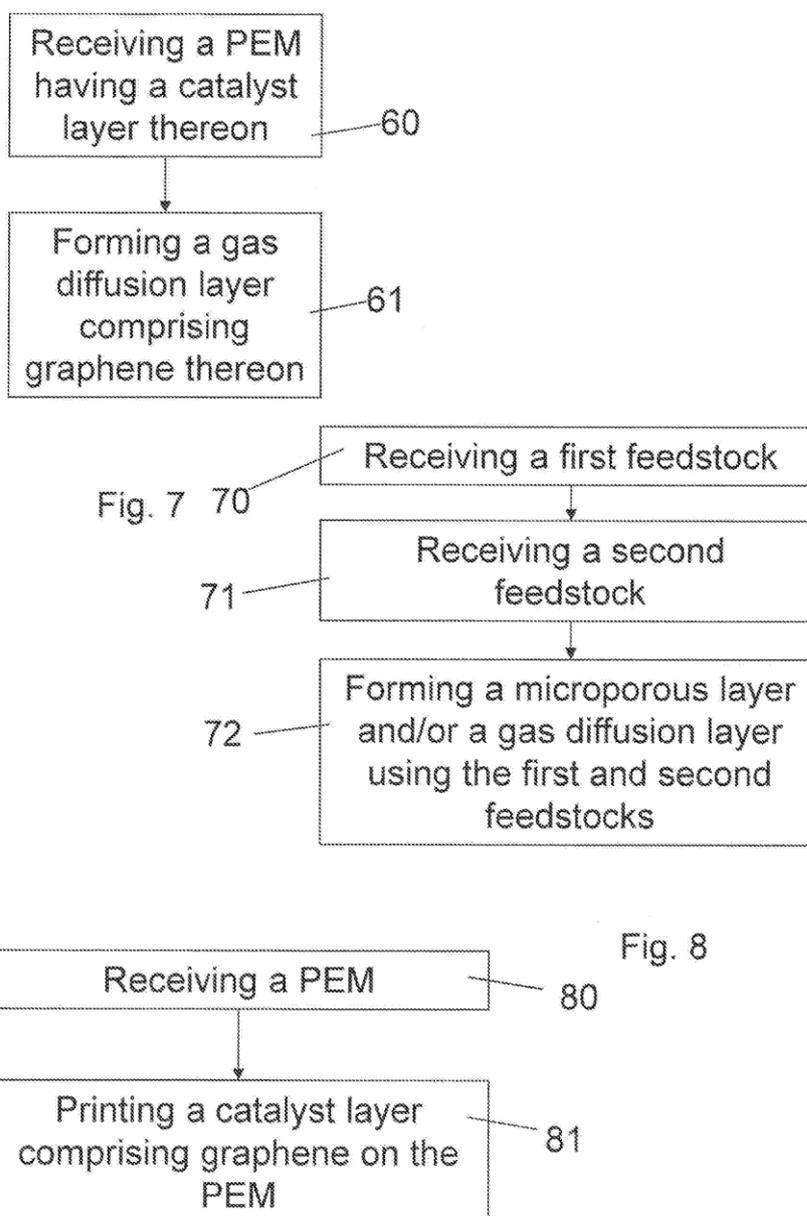


Figure 11.6. Example method of forming a catalyst layer



11.12. MULTILAYERED COMPOSITE PROTON EXCHANGE MEMBRANE AND A PROCESS FOR MANUFACTURING THE SAME

Patent number: **US9023553B2**

Priority date: 2007-09-04

ABSTRACT

A multilayered membrane for use with fuel cells and related applications. The multilayered membrane includes a carrier film, at least one layer of an undoped conductive polymer electrolyte material applied onto the carrier film, and at least one layer of a conductive polymer electrolyte material applied onto the adjacent layer of polymer electrolyte material. Each layer of conductive polymer electrolyte material is doped with a plurality of nanoparticles. Each layer of undoped electrolyte material and doped electrolyte material may be applied in an alternating configuration, or alternatively, adjacent layers of doped conductive polymer electrolyte material is employed. The process for producing a multilayered composite membrane includes providing a carrier substrate and solution casting a layer of undoped conductive polymer electrolyte material and a layer of conductive polymer electrolyte material doped with nanoparticles in an alternating arrangement or in an arrangement where doped layers are adjacent to one another.

CLAIMS (66)

We claim:

1. A multi-layered composite solution cast membrane comprising a sandwich configuration of layers, said sandwich configuration of layers comprising: a bottom layer of unfilled conductive polymer electrolyte material having a top side and a bottom side, said bottom layer of unfilled conductive polymer electrolyte material having a dry thickness in the range 5-20 microns for providing mechanical strength to said multi-layered composite solution cast membrane; a first layer of a doped conductive polymer electrolyte material having a top side and a bottom side, said first layer of a doped conductive polymer electrolyte material being adjacent to said bottom layer at the top side of said of said bottom layer, said first layer of doped conductive polymer electrolyte material having a dry thickness in the range of 5-20 microns and being doped with a plurality of nanoparticles for internal water management of the membrane to achieve a managed level hydration, wherein said plurality of nanoparticles comprises about 0.1% wt. to no more than about 50% wt. based on the dry weight of said first layer of a doped conductive polymer electrolyte material, and wherein said first layer of said doped conductive polymer electrolyte material contains no voids; a second layer an unfilled conductive polymer electrolyte material having a top side and a bottom side, said second layer of unfilled conductive polymer electrolyte material being adjacent to said first layer of doped conductive polymer electrolyte material at the top side of said



of said first layer of doped conductive polymer electrolyte material, said second layer of unfilled conductive polymer electrolyte material having a dry thickness in the range 5-20 microns for providing mechanical strength to said multi-layered composite solution cast membrane; a second layer of a doped conductive polymer electrolyte material having a top side and a bottom side, said second layer of a doped conductive polymer electrolyte material being adjacent to said second layer of unfilled conductive polymer electrolyte material at the top side of said of said second layer of unfilled conductive polymer electrolyte material, said second layer of doped conductive polymer electrolyte material having a dry thickness in the range of 5-20 microns and being doped with a plurality of nanoparticles for internal water management of the membrane to achieve a managed level hydration, wherein said plurality of nanoparticles comprises about 0.1% wt. to no more than about 50% wt. based on the dry weight of said first layer of a doped conductive polymer electrolyte material, and wherein said second layer of said doped conductive polymer electrolyte material contains no voids; and a top layer of an unfilled conductive polymer electrolyte material adjacent to said second layer of a doped conductive polymer electrolyte material at the top side of said second layer of a doped conductive polymer electrolyte material, said top layer of unfilled conductive polymer electrolyte material having a dry thickness in the range 5-20 microns for providing mechanical strength to said multi-layered composite solution cast membrane; wherein said unfilled layers and said doped layers comprise a material selected from the group consisting of perfluorosulfonic acid (PFSA) and sulfonated polyphenylsulfone polyers, wherein said nanoparticles comprise at least one selected from the group consisting of zirconium sulphophenyl phosphate and a silsesquioxane cage structure compound and wherein said plurality of nanoparticles are doped in a concentration of from about 0.05-50% in said layers of a doped conductive polymer electrolyte material relative to the other layers of said multi-layer conductive polymer electrolyte material.

2. The multi-layered composite solution cast membrane according to claim 1, wherein said plurality of nanoparticles comprise a distribution selected from the group consisting of hydrophilic nano-sized zirconium sulphophenyl phosphonate particles and sulfonated polyhedral oligomeric silsesquioxane particles.
3. The multi-layered composite solution cast membrane according to claim 1, further comprising a temporary carrier film adjacent to said bottom layer of unfilled conductive polymer electrolyte material on the side opposite that adjacent to said first layer of doped conductive polymer electrolyte material, said temporary carrier film for supporting the balance of said multi-layered solution cast composite membrane during processing of said multi-layered composite solution cast membrane.
4. The multilayered composite solution cast membrane according to claim 3, wherein said temporary carrier film comprises a material selected from the group consisting of a polyester material, aluminum foil polyethylene coated papers, casting papers comprising a specialty high temperature coating being devoid of polyethylene, casting papers having high release silicones and aluminum foil laminates with stable paper substrates.
5. The multilayered composite solution cast membrane according to claim 4, wherein said polyester material is selected from the group consisting of polyethylene terephthalate (PET) and biaxially-oriented polyethylene terephthalate.
6. The multilayered composite solution cast membrane according to claim 1, wherein said layers of doped conductive polymer electrolyte material contain sulfonic acid groups.
7. The multilayered composite solution cast membrane according to claim 1, wherein said multilayered composite membrane comprises a total amount of layers in the range of 3-9 layers and comprises a total thickness in the range of 15-180 microns.



8. The multilayered composite solution cast membrane according to claim 1, wherein each individual layer of said multilayered composite membrane comprises a dry thickness in the range of between 5-20 microns.
9. A multilayered composite solution cast membrane consisting of:
 - a temporary carrier film for supporting the balance of said multilayered solution cast composite membrane during processing of said multilayered composite solution cast membrane; at least one layer of an unfilled conductive polymer electrolyte material, wherein one layer of said at least one layer of unfilled conductive polymer electrolyte material is adjacent to said temporary carrier film, and wherein each layer of said at least one layer of unfilled conductive polymer electrolyte material comprises a dry thickness in the range 5-20 microns for providing mechanical strength to said multilayered composite solution cast membrane; at least one layer of a doped conductive polymer electrolyte material adjacent to said respective at least one layer of conductive polymer electrolyte material, each layer of said doped conductive polymer electrolyte material having a dry thickness in the range of 5-20 microns and being doped with a plurality of nanoparticles for internal water management of the membrane to achieve a managed level hydration, wherein said plurality of nanoparticles comprise about 0.1% wt. to no more than about 50% wt. based on the dry weight of said at least one layer of conductive polymer electrolyte material, and wherein each layer of said at least one layer of doped conductive polymer electrolyte material contains no voids; and a top layer of conductive polymer electrolyte material having a dry thickness in the range 5-20 microns for providing mechanical strength to said multilayered composite solution cast membrane.
10. The multilayered composite solution cast membrane according to claim 9, wherein said at least one layer of unfilled conductive polymer electrolyte material and said at least one layer of doped conductive polymer electrolyte material are provided in an alternating configuration in said multilayered composite membrane.
11. The multilayered composite solution cast membrane according to claim 9, wherein at least two layers of said at least one layer of doped conductive polymer electrolyte material are provided adjacent to each other in said multilayered composite membrane.
12. The multilayered composite solution cast membrane according to claim 9, wherein said top layer of conductive polymer electrolyte material is a material selected from the group consisting of perfluorosulfonic acid (PFSA) and sulfonated polyphenylsulfone polymers, said top layer of conductive polymer electrolyte material being adjacent to the final layer of said at least one layer of doped conductive polymer electrolyte material.
13. The multilayered composite solution cast membrane according to claim 9, wherein said temporary carrier film comprises a material selected from the group consisting of a polyester material, aluminum foil polyethylene coated papers, casting papers comprising a specialty high temperature coating being devoid of polyethylene, casting papers having high release silicones and aluminum foil laminates with stable paper substrates.
14. The multilayered composite solution cast membrane according to claim 13, wherein said polyester material is selected from the group consisting of polyethylene terephthalate (PET) and biaxially-oriented polyethylene terephthalate.
15. The multilayered composite solution cast membrane according to claim 9, wherein said at least one layer of doped conductive polymer electrolyte material is selected from the group consisting of perfluorosulfonic acid (PFSA), and sulfonated polyphenylsulfone polymers.
16. The multilayered composite solution cast membrane according to claim 15, wherein said at least one layer of doped conductive polymer electrolyte material contains sulfonic acid groups.



17. The multilayered composite solution cast membrane according to claim 16, wherein said at least one layer of doped conductive polymer electrolyte material is selected from the group consisting of perfluorosulfonic acid (PFSA), and sulfonated polyphenylsulfone polymers.
18. The multilayered composite solution cast membrane according to claim 9, wherein said plurality of nanoparticles comprise at least one selected from the group consisting of zirconium sulphophenyl phosphate and a silsesquioxane cage structure compound.
19. The multilayered composite solution cast membrane according to claim 18, wherein said plurality of nanoparticles comprise a distribution selected from the group consisting of hydrophilic nano-sized zirconium sulphophenyl phosphonate particles and sulfonated polyhedral oligomeric silsesquioxane particles.
20. The multilayered composite solution cast membrane according to claim 9, wherein said top layer of a conductive polymer electrolyte material and said at least one layer of doped conductive polymer electrolyte material comprise the same material.
21. The multilayered composite solution cast membrane according to claim 9, wherein said multilayered composite membrane comprises a total amount of layers in the range of 3-9 layers and comprises a total thickness in the range of 15-180 microns.
22. The multilayered composite solution cast membrane according to claim 9, wherein each individual layer of said multilayered composite membrane comprises a dry thickness in the range of between 5-20 microns.
23. The multilayered composite solution cast membrane according to claim 9, wherein said plurality of nanoparticles are doped in a concentration of from about 0.05-50% in at least one layer of doped conductive polymer electrolyte material relative to the other layers of said doped conductive polymer electrolyte material.
24. A process for producing a multilayered composite solution cast membrane consisting of: a temporary carrier film for supporting the balance of said multilayered solution cast composite membrane during processing of said multilayered composite solution cast membrane; at least one layer of an unfilled conductive polymer electrolyte material, wherein one layer of said at least one layer of unfilled conductive polymer electrolyte material is adjacent to said temporary carrier film, and wherein each layer of said at least one layer of unfilled conductive polymer electrolyte material comprises a dry thickness in the range 5-20 microns for providing mechanical strength to said multilayered composite solution cast membrane; at least one layer of a doped conductive polymer electrolyte material adjacent to said respective at least one layer of conductive polymer electrolyte material, each layer of said doped conductive polymer electrolyte material having a dry thickness in the range of 5-20 microns and being doped with a plurality of nanoparticles for internal water management of the membrane to achieve a managed level hydration, wherein said plurality of nanoparticles comprise about 0.1% wt. to no more than about 50% wt. based on the dry weight of said at least one layer of conductive polymer electrolyte material, and wherein each layer of said at least one layer of doped conductive polymer electrolyte material contains no voids; and a top layer of conductive polymer electrolyte material having a dry thickness in the range 5-20 microns for providing mechanical strength to said multilayered composite solution cast membrane, said process comprising the steps of: providing said temporary carrier film for supporting the balance of said multilayered composite solution cast membrane; solution casting a solution of unfilled conductive polymer electrolyte material to said temporary carrier film for forming said at least one layer of unfilled conductive polymer electrolyte material, wherein said soluble unfilled conductive polymer electrolyte material is selected from the group consisting of a crystalline material, a semi-crystalline material and an amorphous material; drying said at least one layer of unfilled conductive polymer



- electrolyte material; applying a soluble solution of doped conductive polymer electrolyte material and nanoparticles to said at least one layer of unfilled conductive polymer electrolyte material for forming said at least one layer of doped conductive polymer electrolyte material; drying said at least one layer of doped conductive polymer electrolyte material; solution casting a solution of unfilled conductive polymer electrolyte material to said at least one layer of doped conductive polymer electrolyte material for forming at least one additional layer of unfilled conductive polymer electrolyte material; drying said at least one additional layer of unfilled conductive polymer electrolyte material; solution casting a solution of doped conductive polymer electrolyte material and nanoparticles to said at least one additional layer of unfilled conductive polymer electrolyte material for forming at least one additional layer of doped conductive polymer electrolyte material; and drying said at least one additional layer of doped conductive polymer electrolyte material.
25. The process according to claim 24, wherein said process comprises solution casting said at least one additional layer of unfilled conductive polymer electrolyte material and said at least one additional layer of doped conductive polymer electrolyte material in an alternating configuration, for forming each of said at least one layer of unfilled conductive polymer electrolyte material, said at least one additional layer of unfilled conductive polymer electrolyte material, said at least one layer of doped conductive polymer electrolyte material and said at least one additional layer of doped conductive polymer electrolyte material.
26. The process according to claim 24, wherein said process comprises the step of solution casting at least two layers of said at least one layer of doped conductive polymer electrolyte material in an adjacent arrangement.
27. The process according to claim 24, wherein said solution casting steps are selected from the group consisting of **gravure coating**, **reverse gravure coating**, direct coating, offset coating, micro coating, knife over roll coating, reverse roll coating, slot die coating, **micro gravure coating**, spray coating and curtain coating.
28. The process according to claim 24, further comprising the steps of: solution casting a solution of undoped conductive polymer electrolyte material to the top layer of said at least one additional layer of doped conductive polymer electrolyte material for forming a top layer of unfilled conductive polymer electrolyte material, wherein said soluble unfilled conductive polymer electrolyte material is selected from the group consisting of a crystalline material, a semi-crystalline material and an amorphous material; and drying said top layer of unfilled conductive polymer electrolyte material.
29. The process according to claim 28, wherein said solution casting step is selected from the group consisting of **gravure coating**, **reverse gravure coating**, direct coating, offset coating, micro coating, knife over roll coating, reverse roll coating, slot die coating, **micro gravure coating**, spray coating and curtain coating.
30. The process according to claim 24, further comprising the step of annealing said multilayered composite membrane when said layers comprise a material selected from the group consisting of a crystalline material and a semi-crystalline material.
31. The process according to claim 24, further comprising the step of drying said multilayered composite membrane when said layers comprise an amorphous material.
32. The process according to claim 31, wherein said drying step is selected from the group consisting of drying in a convection oven and air-drying, when said layers comprise an amorphous material.
33. The process according to claim 24, wherein said temporary carrier film comprises a material selected from the group consisting of a polyester material, glass, aluminum foil having a thickness in the range of 25-100 microns, polyester coated papers, casting papers comprising a specialty high



- temperature coating and being devoid of polyester, casting papers having high release silicones and aluminum foil laminates with stable paper substrates.
34. The process according to claim 33, wherein said polyester material is selected from the group consisting of polyethylene terephthalate (PET) and biaxially-oriented polyethylene terephthalate.
 35. The process according to claim 24, wherein said at least one layer of unfilled conductive polymer electrolyte material, said at least one additional layer of unfilled conductive polymer electrolyte material and said top layer of unfilled conductive polymer electrolyte material comprise a material selected from the group consisting of perfluorosulfonic acid (PFSA), polyphenylsulfone and tetrafluorethylene copolymers.
 36. The process according to claim 24, wherein said at least one layer of doped conductive polymer electrolyte material and said at least one additional layer of doped conductive polymer electrolyte material comprise a material selected from the group consisting of perfluorosulfonic acid (PFSA), polyphenylsulfone and tetrafluorethylene copolymers.
 37. The process according to claim 24, wherein said solvent is at least one solvent selected from the group consisting of water, alcohols, aromatics, acetates, N,N-dimethylacetamide (DMAC), tetrahydrofuran (THF), a diethyl ether, N-methylpyrrolidone (NMP), methylene chloride, ketones, and dimethyl sulfoxide (DMSO).
 38. The process according to claim 37, wherein said N,N-dimethylacetamide (DMAC) is selected from the group consisting of acetic acid, dimethylamide; dimethyl acetamide and acetyldimethylamine.
 39. The process according to claim 24, wherein each of said solution-casting steps comprise solution casting of polymers wherein said solvent is a mixture of at least two true solvents and/or a mixture of at least one true solvent and at least one diluent, wherein said at least one diluent is selected from the group consisting of a low molecular weight alcohol, an aromatic and an acetate.
 40. The process according to claim 24, wherein said plurality of nanoparticles is at least one selected from the group consisting of zirconium dioxide, zirconium oxides, clays, zeolites, silica, compounds of silica, and titanium dioxide.
 41. The process according to claim 40, wherein said plurality of nanoparticles comprises a distribution selected from the group consisting of hydrophilic nano-sized zirconium phosphate/phosphonate particles and sulfonated polyhedral oligomeric silsesquioxane.
 42. The process according to claim 40, wherein said plurality of nanoparticles comprises a distribution selected from the group consisting of hydrophilic nano-sized zirconium phosphate/phosphonate particles and sulfonated polyhedral oligomeric silsesquioxane.
 43. The process according to claim 24, wherein said at least one layer of unfilled conductive polymer electrolyte material, said at least one additional layer of unfilled conductive polymer electrolyte material and said top layer of a unfilled conductive polymer electrolyte material comprise the same material.
 44. The process according to claim 24, wherein said multilayered composite membrane comprises a total amount of layers in the range of 3-9 layers and comprises a total thickness in the range of 15-180 microns.
 45. The process according to claim 24, wherein said process comprises the step of doping said plurality of nanoparticles in a uniform concentration or in varying concentrations in said at least one layer of doped conductive polymer electrolyte material relative to the other doped layers of said multilayered conductive membrane.
 46. The process according to claim 24, wherein the concentration of said plurality of nanoparticles in each doped layer of said multilayered conductive membrane is the same or different.



47. A process for producing a multilayered composite solution cast membrane comprising a sandwich configuration of layers, said sandwich configuration of layers comprising: a bottom layer of unfilled conductive polymer electrolyte material having a top side and a bottom side, said bottom layer of unfilled conductive polymer electrolyte material having a dry thickness in the range 5-20 microns for providing mechanical strength to said multi-layered composite solution cast membrane; a first layer of a doped conductive polymer electrolyte material having a top side and a bottom side, said first layer of a doped conductive polymer electrolyte material being adjacent to said bottom layer at the top side of said of said bottom layer, said first layer of doped conductive polymer electrolyte material having a dry thickness in the range of 5-20 microns and being doped with a plurality of nanoparticles for internal water management of the membrane to achieve a managed level hydration, wherein said plurality of nanoparticles comprises about 0.1% wt. to no more than about 50% wt. based on the dry weight of said first layer of a doped conductive polymer electrolyte material, and wherein said first layer of said doped conductive polymer electrolyte material contains no voids; a second layer an unfilled conductive polymer electrolyte material having a top side and a bottom side, said second layer of unfilled conductive polymer electrolyte material being adjacent to said first layer of doped conductive polymer electrolyte material at the top side of said of said first layer of doped conductive polymer electrolyte material, said second layer of unfilled conductive polymer electrolyte material having a dry thickness in the range 5-20 microns for providing mechanical strength to said multi-layered composite solution cast membrane; a second layer of a doped conductive polymer electrolyte material having a top side and a bottom side, said second layer of a doped conductive polymer electrolyte material being adjacent to said second layer of unfilled conductive polymer electrolyte material at the top side of said of said second layer of unfilled conductive polymer electrolyte material, said second layer of doped conductive polymer electrolyte material having a dry thickness in the range of 5-20 microns and being doped with a plurality of nanoparticles for internal water management of the membrane to achieve a managed level hydration, wherein said plurality of nanoparticles comprises about 0.1% wt. to no more than about 50% wt. based on the dry weight of said first layer of a doped conductive polymer electrolyte material, and wherein said second layer of said doped conductive polymer electrolyte material contains no voids; and a top layer of an unfilled conductive polymer electrolyte material adjacent to said second layer of a doped conductive polymer electrolyte material at the top side of said second layer of a doped conductive polymer electrolyte material, said top layer of unfilled conductive polymer electrolyte material having a dry thickness in the range 5-20 microns for providing mechanical strength to said multi-layered composite solution cast membrane; wherein said unfilled layers and said doped layers comprise a material selected from the group consisting of perfluorosulfonic acid (PFSA) and sulfonated polyphenylsulfone polymers, wherein said nanoparticles comprise at least one selected from the group consisting of zirconium sulphophenyl phosphate and a silsesquioxane cage structure compound and wherein said plurality of nanoparticles are doped in a concentration of from about 0.05-50% in said layers of a doped conductive polymer electrolyte material relative to the other layers of said multi-layer conductive polymer electrolyte material, said process comprising the steps of: providing a temporary carrier film for supporting the balance of said multilayered composite membrane; solution casting a solution of unfilled conductive polymer electrolyte material to said temporary carrier film for forming said bottom layer of unfilled conductive polymer electrolyte material; drying said bottom layer of unfilled conductive polymer electrolyte material; applying a soluble solution of conductive polymer electrolyte material and nanoparticles to said bottom layer of unfilled conductive polymer electrolyte material for forming a first layer of doped conductive polymer electrolyte material;



- drying said first layer of doped conductive polymer electrolyte material; solution casting a solution of unfilled conductive polymer electrolyte material to said bottom layer of doped conductive polymer electrolyte material for forming said second layer of unfilled conductive polymer electrolyte material; drying said second layer of unfilled conductive polymer electrolyte material; solution casting a solution of doped conductive polymer electrolyte material and nanoparticles to said second layer of unfilled conductive polymer electrolyte material for forming said second layer of doped conductive polymer electrolyte material; and drying said second layer of doped conductive polymer electrolyte material.
48. The process according to claim 47, wherein said process comprises solution casting said layers.
 49. The process according to claim 47, wherein said solution casting steps are selected from the group consisting of **gravure coating**, **reverse gravure coating**, direct coating, offset coating, micro coating, knife over roll coating, reverse roll coating, slot die coating, **micro gravure coating**, spray coating and curtain coating.
 50. The process according to claim 47, further comprising the steps of: solution casting a solution of unfilled conductive polymer electrolyte material to said second layer of doped conductive polymer electrolyte material for forming a top layer of unfilled conductive polymer electrolyte material; and drying said top layer of unfilled conductive polymer electrolyte material.
 51. The process according to claim 50, wherein said solution casting step is selected from the group consisting of **gravure coating**, **reverse gravure coating**, direct coating, offset coating, micro coating, knife over roll coating, reverse roll coating, slot die coating, **micro gravure coating**, spray coating and curtain coating.
 52. The process according to claim 47, further comprising the step of annealing said multilayered composite membrane when said layers comprise a material selected from the group consisting of a crystalline material and a semi-crystalline material.
 53. The process according to claim 47, further comprising the step of drying said multilayered composite membrane when said layers comprise an amorphous material.
 54. The process according to claim 53, wherein said drying step is selected from the group consisting of drying in a convection oven and air-drying.
 55. The process according to claim 47, wherein said temporary carrier film comprises a material selected from the group consisting of a polyester material, glass, aluminum foil having a thickness in the range of 25-100 microns, polyester coated papers, casting papers comprising a specialty high temperature coating and being devoid of polyester, casting papers having high release silicones and aluminum foil laminates with stable paper substrates.
 56. The process according to claim 55, wherein said polyester material is selected from the group consisting of polyethylene terephthalate (PET) and biaxially-oriented polyethylene terephthalate.
 57. The process according to claim 47, wherein said layers of unfilled conductive polymer electrolyte material comprise a material selected from the group consisting of perfluorosulfonic acid (PFSA), polyphenylsulfone and tetrafluoroethylene copolymers.
 58. The process according to claim 47, wherein said layers of doped conductive polymer electrolyte material comprise a material selected from the group consisting of perfluorosulfonic acid (PFSA), polyphenylsulfone and tetrafluoroethylene copolymers.
 59. The process according to claim 47, wherein said solvent is at least one solvent selected from the group consisting of water, alcohols, aromatics, acetates, N,N-dimethylacetamide (DMAC), tetrahydrofuran (THF), a diethyl ether, N-methylpyrrolidone (NMP), methylene chloride, ketones, and dimethyl sulfoxide (DMSO).



60. The process according to claim 59, wherein said N,N-dimethylacetamide (DMAC) is selected from the group consisting of acetic acid, dimethylamide; dimethyl acetamide and acetyldimethylamine.
61. The process according to claim 47, wherein each of said solution-casting steps comprises solution casting of polymers wherein said solution is a mixture of at least two true solvents and/or a mixture of at least one true solvent and at least one diluent, wherein said at least one diluent is selected from the group consisting of a low molecular weight alcohol, an aromatic and an acetate.
62. The process according to claim 47, wherein said plurality of nanoparticles is at least one selected from the group consisting of zirconium dioxides, zirconium oxides, clays, zeolites, silica, compounds of silica, and titanium dioxide.
63. The process according to claim 47, wherein said layers of unfilled conductive polymer electrolyte material comprise the same material.
64. The process according to claim 47, wherein said multilayered composite membrane comprises a total amount of layers in the range of 3-9 layers and comprises a total thickness in the range of 15-180 microns.
65. The process according to claim 47, wherein said process comprises the step of doping said plurality of nanoparticles in a uniform concentration or in varying concentrations in said layers of doped conductive polymer electrolyte material relative to the other doped layers.
66. The process according to claim 47, wherein the concentration of said plurality of nanoparticles in each doped layer is the same or different.

11.13. STRUCTURES AND METHODS OF MANUFACTURE FOR GAS DIFFUSION ELECTRODES AND ELECTRODE COMPONENTS

PATENT NUMBER: US6103077A

PRIORITY DATE: 1998-01-02

ABSTRACT

Gas Diffusion Electrodes (GDES) play a pivotal role in clean energy production as well as in electrochemical processes and sensors. These gas-consuming electrodes are typically designed for liquid electrolyte systems such as phosphoric acid and alkaline fuel cells, and are commercially manufactured by hand or in a batch process. However, GDEs using the new electrolytes such as conductive polymer membranes demand improved electrode structures.

This invention pertains to GDEs and gas diffusion media with new structures for systems using membrane electrode assemblies (MEAs), and automated methods of manufacture that lend themselves to continuous mass production. Unexpected improvements in gas and vapor transport through the electrode are realized by incorporating a new dispersion process in the construction, reformulating the applied mix with solution additives, and creating a novel coating structure on a conductive web. Furthermore, combining these changes with a judicious choice in coating methodology allows one to produce these materials in a continuous, automated fashion.



CLAIMS (24)

What we claim is:

1. A gas diffusion electrode comprising an electrically conductive web provided on at least one side with a layer comprising a homogeneous dispersion of carbon black.
2. The electrode of claim 1 wherein the electrically conductive web is a carbon cloth web and the layer is provided with an electrocatalyst.
3. The electrode of claim 2 wherein the layer electrocatalyst is platinum.
4. The electrode of claim 1 wherein the layer contains 0.5 to 5 mg/cm² of carbon black.
5. The electrode of claim 1 wherein the layer further contains polytetrafluoroethylene.
6. A membrane electrode assembly comprising an ion exchange membrane against the coated side of a gas diffusion electrode of claim 1.
7. In a fuel cell, the improvement comprising using the membrane electrode assembly of claim 6.
8. A method of manufacturing an electrode of claim 1 comprising
 - a) preparing a first dispersion mixture of a first carbon black by means of a homogenizer,
 - b) adding a binder to the resulting mixture,
 - c) adding at least one dispersion-stabilizing substance to the mixture,
 - d) applying at least one coat of said first dispersion mixture to an electrically conductive web by using at least one **gravure coating head**,
 - e) drying said first dispersion mixture on the web, and
 - f) sintering the resulting electrode at 300-400° C.
9. The method of claim 8 wherein said first carbon black in said first dispersion mixture is hydrophobic.
10. The method of claim 9 wherein after said drying of said first dispersion mixture on the web and before said sintering of said resulting electrode, a coat of a second dispersion mixture containing a second black is applied and then dried.
11. The method of claim 10 wherein said second carbon black of said second dispersion mixture is hydrophilic.
12. The method of claim 11 wherein said second hydrophilic carbon black is a support for at least one of the group consisting of platinum group metals, platinum group metal oxides, alloys and mixtures thereof.
13. The method of claim 8 wherein said first carbon black in said first dispersion mixture is hydrophilic.
14. The method of claim 13 wherein said first hydrophilic carbon black is a support for at least one member of the group consisting of platinum group metals, platinum group metal oxides, alloys and mixtures thereof.
15. The method of manufacturing of claim 8 wherein said at least one stabilizing substance is selected from the group consisting of chlorofluorocarbons, polychlorotrifluoroethylene, polyvinyl alcohol, ethylene glycol, polyethylene glycol alkyl ether, polyoxyethylene, non-ionic surfactants, primary alcohol alkoxylates, polyoxyethylene sorbitan mono-oleate, acrylic emulsions, sodium polyacrylate and naphthalene-formaldehyde condensate sulphonates.
16. A method of manufacturing an electrode of claim 1 comprising
 - a) preparing a first dispersion mixture of a first carbon black by means of a homogenizer,
 - b) adding a binder to the resulting mixture,
 - c) adding at least one dispersion-stabilizing substance to the mixture,
 - d) applying at least one coat of said first dispersion mixture to an electrically conductive web by using at least one slot-die coating head,



- e) drying said first dispersion mixture on the web, and
- f) sintering the resulting electrode at 300-400° C.
- 17. The method of claim 16 wherein said carbon black in said first dispersion mixture is hydrophobic.
- 18. The method of claim 17 wherein after said drying of said first dispersion mixture on the web and before said sintering of said resulting electrode, a coat of a second dispersion mixture containing a second carbon black is applied and then dried.
- 19. The method of claim 18 wherein the second carbon black of said second dispersion mixture is hydrophilic.
- 20. The method of claim 19 wherein said second hydrophilic carbon black is a support for at least one member of the group consisting of platinum group metals, platinum group metal oxides, alloys and mixtures thereof.
- 21. The method of claim 16 wherein said first carbon black in said first dispersion mixture is hydrophilic.
- 22. The method of claim 21 wherein said first hydrophilic carbon black is a support for at least one member of the group consisting of platinum group metals, platinum group metal oxides, alloys and mixtures thereof.
- 23. The method of manufacturing of claim 16 wherein said at least one stabilizing substance is selected from the group consisting of chlorofluorocarbons, polychlorotrifluoroethylene, polyvinyl alcohol, ethylene glycol, polyethylene glycol alkylether, polyoxyethylene, non-ionic surfactants, primary alcohol alkoxylates, polyoxyethylene sorbitan mono-oleate, acrylic emulsions, sodium polyacrylate and naphthalene-formaldehyde condensate sulphonates.
- 24. An electrode of claim 1 wherein the resistance to flow is from 0.06 to 0.005 LPM/cm H₂ O/cm².



11.14. METHOD FOR PRODUCING CATALYST LAYERS FOR FUEL CELLS

Patent number: **WO2014155901A1**

Priority date: **2013-03-28**

ABSTRACT

The present invention relates to a method for producing fuel cell components, in particular a **gravure printing method** for producing catalyst layers, electrodes and membrane electrode units ("MEUs") for polymer electrolyte membrane fuel cells ("PEM fuel cells").

CLAIMS (18)

A **gravure printing method** for producing catalyst layers on substrate materials using a catalyst-containing ink, a printing plate being used which has at least one print image with an interrupted line screen whose longitudinal lines are arranged at an angle α of from 10° to 80° , preferably at an angle α of from 20° to 70° , relative to the printing direction, said print image having a dip volume in the range from 100 to 300 ml/m².

The method as claimed in claim 1, the print image having a dip volume in the range from 150 to 250 ml/m².

The method as claimed in claim 1 or 2, the print image having etch depths in the range from 100 to 250 μm , preferably in the range from 120 to 200 μm .

The method as claimed in any of claims 1 to 3, the catalyst layers produced having a dry layer thickness in the range from 1 to 20 μm , preferably in the range from 2 to 15 μm .

The method as claimed in any of claims 1 to 4, the longitudinal lines of the line screen having line lengths L in the range from 0.1 to 20 mm and line widths B in the range from 0.05 to 0.5 mm.

The method as claimed in any of claims 1 to 5, the interrupted line screen having at least one intermediate space Z between two lines of a row, whose dimensions are in the range from 0.1 to 20 mm.

The method as claimed in any of claims 1 to 6, the print image having a line screen with additional transverse lines, the transverse lines having line lengths (QL) in the range from 0.1 mm to 4.5 mm and which are arranged at an angle β in the range from 5° to 175° relative to the longitudinal lines.

The method as claimed in any of claims 1 to 7, the interrupted line having a screen ruling from 5 L/cm to 20 L/cm.

The method as claimed in any of claims 1 to 8, the catalyst layers produced having a low surface roughness and the Ra value being $< 10\%$ of the respective dry layer thickness.

The method as claimed in any of claims 1 to 9, the substrate materials used being ionomer membranes (in supported or unsupported form), composite membranes, laminated membranes, multilayer membranes, treated or untreated plastics films (such as, for example, polyesters, polyamides or polyimides), transfer picture substrates, decal substrates, coated or treated papers, laminated films and carbon fiber substrates (such as, for example, carbon fiber webs, woven carbon fiber fabrics or carbon fiber papers).



The method as claimed in any of claims 1 to 10, the catalyst-containing ink comprising at least one electrocatalyst, at least one ionomer and at least one solvent.

The method as claimed in any of claims 1 to 11, the catalyst-containing ink having a solids content in the range from 3 to 20% by weight (measured as loss on drying at 120°C/60 minutes).

The method as claimed in any of claims 1 to 12, the catalyst-containing ink having a viscosity in the range from 50 to 1.000 mPa·s, preferably in the range from 150 to 400 mPa·s (measured using a plate/cone system).

The method as claimed in any of claims 1 to 13, the ink supply being effected via a chambered doctor blade system

The method as claimed in any of claims 1 to 14, characterized in that it is effected continuously, preferably in a roll-to-roll method.

The method as claimed in any of claims 1 to 15, the printing speed being in the range from 0.02 to 3 m/s.

The method as claimed in any of claims 1 to 16 said method being used for producing electrodes and membrane electrode units for fuel cells.

A **gravure printing plate** for producing catalyst layers on substrate materials, characterized in that it has at least one print image with an interrupted line screen whose longitudinal lines are arranged at an angle α of from 10° to 80°, preferably at an angle α of from 20° to 70°, relative to the printing direction, said print image having a dip volume in the range from 100 to 300 ml/m².

CLAIMS (18)

A **gravure printing** method for producing catalyst layers on substrate materials using a catalyst-containing ink, a printing plate being used which has at least one print image with an interrupted line screen whose longitudinal lines are arranged at an angle α of from 10° to 80°, preferably at an angle α of from 20° to 70°, relative to the printing direction, said print image having a dip volume in the range from 100 to 300 ml/m².

The method as claimed in claim 1, the print image having a dip volume in the range from 150 to 250 ml/m².

The method as claimed in claim 1 or 2, the print image having etch depths in the range from 100 to 250 μ m, preferably in the range from 120 to 200 μ m.

The method as claimed in any of claims 1 to 3, the catalyst layers produced having a dry layer thickness in the range from 1 to 20 μ m, preferably in the range from 2 to 15 μ m.

The method as claimed in any of claims 1 to 4, the longitudinal lines of the line screen having line lengths L in the range from 0.1 to 20 mm and line widths B in the range from 0.05 to 0.5 mm.

The method as claimed in any of claims 1 to 5, the interrupted line screen having at least one intermediate space Z between two lines of a row, whose dimensions are in the range from 0.1 to 20 mm.

The method as claimed in any of claims 1 to 6, the print image having a line screen with additional transverse lines, the transverse lines having line lengths (QL) in the range from 0.1 mm to 4.5 mm and which are arranged at an angle β in the range from 5° to 175° relative to the longitudinal lines.

The method as claimed in any of claims 1 to 7, the interrupted line having a screen ruling from 5 L/cm to 20 L/cm.



The method as claimed in any of claims 1 to 8, the catalyst layers produced having a low surface roughness and the Ra value being < 10% of the respective dry layer thickness.

The method as claimed in any of claims 1 to 9, the substrate materials used being ionomer membranes (in supported or unsupported form), composite membranes, laminated membranes, multilayer membranes, treated or untreated plastics films (such as, for example, polyesters, polyamides or polyimides), transfer picture substrates, decal substrates, coated or treated papers, laminated films and carbon fiber substrates (such as, for example, carbon fiber webs, woven carbon fiber fabrics or carbon fiber papers).

The method as claimed in any of claims 1 to 10, the catalyst-containing ink comprising at least one electrocatalyst, at least one ionomer and at least one solvent.

The method as claimed in any of claims 1 to 11, the catalyst-containing ink having a solids content in the range from 3 to 20% by weight (measured as loss on drying at 120°C/60 minutes).

The method as claimed in any of claims 1 to 12, the catalyst-containing ink having a viscosity in the range from 50 to 1.000 mPa·s, preferably in the range from 150 to 400 mPa·s (measured using a plate/cone system).

The method as claimed in any of claims 1 to 13, the ink supply being effected via a chambered doctor blade system

The method as claimed in any of claims 1 to 14, characterized in that it is effected continuously, preferably in a roll-to-roll method.

The method as claimed in any of claims 1 to 15, the printing speed being in the range from 0.02 to 3 m/s.

The method as claimed in any of claims 1 to 16 said method being used for producing electrodes and membrane electrode units for fuel cells.

A **gravure printing** plate for producing catalyst layers on substrate materials, characterized in that it has at least one print image with an interrupted line screen whose longitudinal lines are arranged at an angle α of from 10° to 80°, preferably at an angle α of from 20° to 70°, relative to the printing direction, said print image having a dip volume in the range from 100 to 300 ml/m².

Figure 1

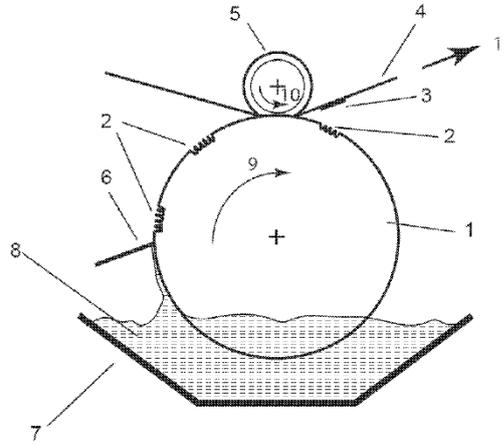
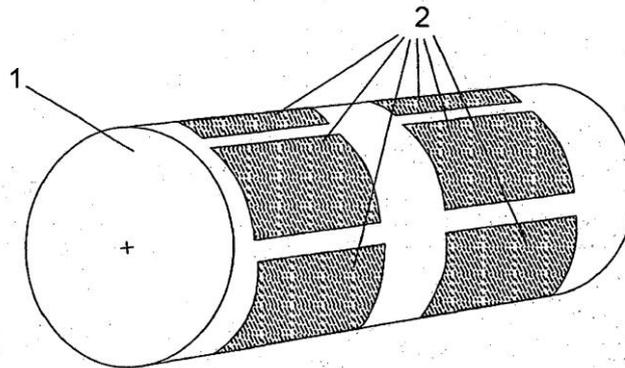


Figure 11.7.

Figure 11.8.
Print images (2) can
be provided on the
printing plate cylinder
(1).

Figure 2





Note: the following patent is not specific for PEMFC. Its name is not cited clearly in the text

11.15. PROCESS FOR GRAVURE PRINTING WITH A WATER-BASED INK

PATENT NUMBER: US20120079952A1

PRIORITY DATE: 2009-06-18

ABSTRACT

Abstract

The present invention consists of a process where a water-based ink is printed using a **gravure** press with a specially engraved cylinder.

CLAIMS (26)

1. **Gravure printing process**, characterized in the use of
 - (a) a water-based **gravure printing ink** composition comprising 5 to 35 wt. % colorant based on the total composition and 40 to 80 wt % water based on the total composition and
 - (b) an engraved cylinder with cells having a stylus angle of the inversed pyramid in a range from 110° to 150° and having a shape corresponding to screen angle type 0, 1, 2, 3 or 4 according to the Hell nomenclature, or having a shape corresponding to screen angles 70/33°, 70/60°, 70/45°, 58/33°, or 100/33° according to the Ohio nomenclature.
2. Process according to claim 1, wherein the colorant is a yellow pigment.
3. Process according to claim 1, wherein the ink composition further comprises as binder a polymer mixture of
 - (1) one or more finely dispersed, aqueous-basic insoluble emulsion (co)polymers (component 1) in intimate admixture with
 - (2) one or more aqueous-basic soluble and/or dispersible (co)polymer compounds with lower molecular weights than that of (1) (component 2)said polymer components (1) and (2) being characterized by their glass transition temperatures (Tg) as follows: Tg(1) is equal to or less than 0° C. and Tg(2) is equal to or higher than 0° C.
4. Process according to claim 1, wherein the ink composition additionally comprises one or more additives selected from surfactants, antifoam agents, stabilizers, fillers, plasticizers, waxes, neutralizing agents, dispersing agents, levelling aids and slip aids.
5. Process according to claim 1, wherein the engraved cylinder has cells having a stylus angle of the inversed pyramid in a range from 120° to 140°.
6. Process according to claim 1, wherein the engraved cylinder has cells having a stylus angle of the inversed pyramid of 130°.
7. Process according to claim 1, wherein the engraved cylinder has cells having a shape corresponding to screen angle type 4 according to the Hell nomenclature, or having a shape corresponding to screen angles 100/33° according to the Ohio nomenclature.



8. Process according to claim 1, wherein the engraved cylinder has cells having a stylus angle of the inversed pyramid of 130° and having a shape corresponding to screen angle type 4 according to the Hell nomenclature, or having a shape corresponding to screen angles $100/33^\circ$ according to the Ohio nomenclature.
9. Process according to claim 1, wherein the engraved cylinder has cells having a stylus angle of the inversed pyramid of 140° and having a shape corresponding to screen angle type 0, 1, or 2 according to the Hell nomenclature, or having a shape corresponding to screen angles $70/33^\circ$, $70/45^\circ$, or $70/60^\circ$ according to the Ohio nomenclature.
10. Process according to claim 1, wherein the inversed pyramid of the cells of the engraved cylinder has a quadrangular base shape.
11. Process according to claim 1, which is a **rotogravure process**.
12. Process according to claim 2, which is a 4-color process wherein a water-based ink composition and an engraved cylinder as defined in claim 1 are used for printing at least one color.
13. Process according to claim 12, wherein the yellow ink is a water-based ink as defined in claim 1 and it is printed by using an engraved cylinder as defined in claim 1.
14. Process according to claim 13, wherein the yellow ink is printed by using an engraved cylinder having cell with a screen angle 4 according to Hell nomenclature and a stylus angle of 130° .
15. Process according to claim 1, wherein the substrate to be printed on is a paper.
16. Use of an engraved cylinder with cells having a stylus angle of the inversed pyramid in a range from 110° to 150° and having a shape corresponding to screen angle type 0, 1, 2, 3 or 4 according to the Hell nomenclature, or having a shape corresponding to screen angles $70/33^\circ$, $70/60^\circ$, $70/45^\circ$, $58/33^\circ$, or $100/33^\circ$ according to the Ohio nomenclature, for **gravure printing**, wherein the ink printed with this cylinder is a water-based **gravure printing ink** composition comprising 5 to 35 wt % colorant based on the total composition and 40 to 80 wt % water based on the total composition.
17. Use of an engraved cylinder as defined in any one of claims 1 and 5 to 10 with a water-based ink as defined in claim 1 for avoiding waviness of the printed paper.
18. Use of a **gravure printing process** according to any one of claims 1 to 15 for avoiding waviness of the printed paper.
19. Process according to claim 3, wherein the ink composition additionally comprises one or more additives selected from surfactants, antifoam agents, stabilizers, fillers, plasticizers, waxes, neutralizing agents, dispersing agents, levelling aids and slip aids.
20. Process according to claim 3, wherein the engraved cylinder has cells having a stylus angle of the inversed pyramid in a range from 120° to 140° .
21. Process according to claim 3, wherein the engraved cylinder has cells having a stylus angle of the inversed pyramid of 130° .
22. Process according to claim 3, wherein the engraved cylinder has cells having a shape corresponding to screen angle type 4 according to the Hell nomenclature, or having a shape corresponding to screen angles $100/33^\circ$ according to the Ohio nomenclature.
23. Process according to claim 3, wherein the engraved cylinder has cells having a stylus angle of the inversed pyramid of 130° and having a shape corresponding to screen angle type 4 according to the Hell nomenclature, or having a shape corresponding to screen angles $100/33^\circ$ according to the Ohio nomenclature.
24. Process according to claim 3, wherein the engraved cylinder has cells having a stylus angle of the inversed pyramid of 140° and having a shape corresponding to screen angle type 0, 1, or 2 according to the Hell nomenclature, or having a shape corresponding to screen angles $70/33^\circ$, $70/45^\circ$, or $70/60^\circ$ according to the Ohio nomenclature.



25. Process according to claim 5, wherein the engraved cylinder has cells having a stylus angle of the inversed pyramid of 140° and having a shape corresponding to screen angle type 0, 1, or 2 according to the Hell nomenclature, or having a shape corresponding to screen angles $70/33^\circ$, $70/45^\circ$, or $70/60^\circ$ according to the Ohio nomenclature.
26. Process according to claim 3, wherein the inversed pyramid of the cells of the engraved cylinder has a quadrangular base shape.



11.16. USE OF DISPERSING AGENTS FOR PREPARING INKS FOR FUEL CELLS

PATENT NUMBER: WO2014118363A1

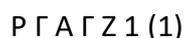
PRIORITY DATE: 2013-02-04

ABSTRACT

The present invention relates to the use of a compound as a dispersing agent in a dispersion including said compound, to at least one catalytic pigment conductor and to at least one solvent, said compound including an aromatic hydrophobic portion and a hydrophilic portion including an anionic end and/or a linear chain including at least 12 -OCH₂CH₂- chain links. The present invention further relates to the use of said compound as a dispersing agent in an ink formulation including said dispersion and a protonic, conducting polymer. The present invention further relates to a dispersion including said compound, suitable for the preparation of an ink formulation for a fuel cell electrode, in particular for a PEMFC, Proton Exchange Membrane Fuel Cell, electrode.

CLAIMS (AUTOMATIC TRANSDUCTION FROM FRENCH)

1. Use of a compound as a dispersant in a dispersion comprising said compound, at least one catalytic pigment conductor and at least one solvent, said compound comprising:
 - An aromatic hydrophobic portion, and
 - A hydrophilic part comprising an anionic end and / or a linear chain comprising at least 12 membered -OCH₂CH₂-.
2. Use according to claim 1, wherein the compound has the formula ABZ, wherein:
 - The A-group represents a phenyl or naphthyl group, optionally substituted with 1 to 5 groups independently selected from the group consisting of alkyl, linear or branched, comprising 1 to 20 carbon atoms, and phenyl, optionally substituted with one or more alkyl, aryl, halogen or haloalkyl,
 - The group -B- represents a single bond or a - (OCH₂CH₂)_n where n is greater than or equal to 12, and
 - The -Z group is selected from the group consisting of OH group and groups -SO₃⁻M⁺, -OSO₃⁻M⁺ and -OP(O)(OH)(O⁻M⁺) wherein M⁺ represents an ion against a positive charge.
3. Use according to claim 1, wherein the compound is of formula (1):

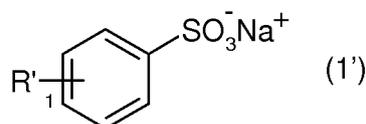


in which :

- The group A represents a phenylene or naphthylene radical optionally substituted by one or more alkyl, aryl, halogen or haloalkyl,
- The group R represents an alkyl group linear or branched comprising from 1 to 20 carbon atoms, optionally substituted by one or more alkyl, aryl, halogen or haloalkyl, and



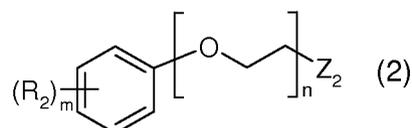
- The $-Z_1$ represents a group $-SO_3^- M^+$, wherein M is an ion against positive charge Use according to claim 3, wherein the compound has the formula.



wherein the group R₁ represents an alkyl group, linear or branched, comprising from 10 to 20 carbon atoms, optionally substituted by one or more alkyl, alkoxy, aryl, halogen or haloalkyl.

5. Use according to claim 4, wherein the group R₁ represents a linear alkyl chain comprising from 10 to 20 carbon atoms.

Use according to claim 1, wherein the compound has the formula



in which :

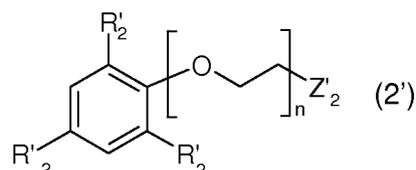
- The $-Z'_2$ group is selected from the group consisting of OH group and groups $-OSO_3^- M^+$ and $-OP(O)(OH)(O^- + M)$ where M⁺ is an against-ion positive charge,

- The R₂ group - represents an alkyl group linear or branched comprising from 1 to 10 carbon atoms, optionally substituted by one or more alkyl, aryl, halogen or haloalkyl,

- N is greater than or equal to 12, and

- M ranges from 0 to 5.

Use according to claim 6, wherein the compound has the formula):

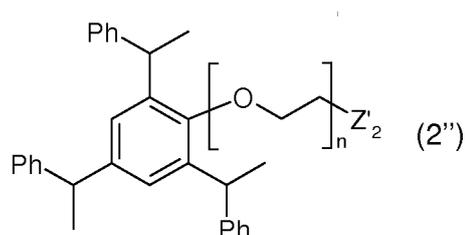


: - in which the group $-Z'_2$ is selected from the group consisting of $-OH$, the group $-OSO_3^- Na^+$ and $-OP(O)(OH)(O^- + M)$ in which M⁺ represents an against-ion with a positive charge,

- The group R₂ represents a linear alkyl group comprising from 1 to 6 carbon atoms, substituted by at least one phenyl group, and

- N is greater than or equal to 12.

8. Use according to claim 7, wherein the compound has the formula (2''):



where in the -Z '2 and n are as defined in claim 7.

9. Dispersion comprising:

- At least one dispersing agent defined in any one of claims 1 to 8,
 - At least one catalytic pigmentosa driver, and
- at least one solvent.

10. The dispersion of claim 9 wherein the solvent is selected from water, an organic solvent, or mixtures thereof.

11. Dispersion according to any one of claims 9 or 10, wherein the catalytic pigment conductor comprises a surface comprising a metal selected from the group consisting of platinum, silver, palladium, ruthenium, nickel, tungsten, cobalt, osmium, molybdenum, titanium, chromium, iron, iridium, gold, tin, and their alloys.

12. Dispersion according to claim 11, wherein the metal is platinum.

13. Dispersion according to any one of claims 9 to 12, wherein the catalytic conductive pigment is in the form of individualized conductive particles or conductive particles aggregates, coated with a metal layer selected from the group consisting of platinum, silver, palladium, ruthenium, nickel, tungsten, cobalt, osmium, molybdenum, titanium, chromium, iron, iridium, gold, of tin, and their alloys.

14. The dispersion of claim 13 wherein the average size of dispersion of individual particles or aggregates of particles is less than 5 μm , preferably less than 2 μm , preferably in the range of 0.1 to 1 μm .

15. Dispersion according to any one of claims 9 to 14, wherein the mass ratio between the dispersant and the pigment catalytic conductor is comprised of 0.3 to 0.5, and preferably approximately equal to 0.4.

16. The ink formulation comprising:

- A dispersion according to any one of claims 9 to 15, and
 - A proton-conducting polymer.
17. The ink formulation according to claim 16, wherein the proton conducting polymer is a perfluorosulfonic acid polymer.

18. The ink formulation according to claim 17, wherein the mass proportion of proton conducting polymer is in the range of 1% to 5% relative to the total weight of the formulation.

19. The ink formulation according to any one of claims 16 to 18, wherein the proportion by weight of liquid phase is from 85% to 98% relative to the total weight of the formulation.

20. The ink formulation according to any one of claims 16 to 18, wherein the proportion by weight of liquid phase is from 60% to 80% relative to the total weight of the formulation. 21. A process for preparing a dispersion according to any one of claims 9 to 15, comprising the steps of: - mixing the solvent, the dispersing agent and the catalytic pigment conductor, and

- Grinding the resulting mixture to obtain said dispersion.



22. A process for preparing an ink formulation according to any one of claims 16 to 20, comprising a step of mixing the proton conducting polymer with a dispersion according to any one of claims 9 to 15.

23. Use of an ink formulation according to any one of claims 16 to 20 for preparing a substrate coated with a layer of catalytic conductive pigment.

24. Use according to claim 23 for preparing a fuel cell electrode with the proton exchange membrane.

25. A method for preparing a substrate coated with a layer of catalytic conductive pigment, comprising the steps of:

- Depositing an ink formulation according to any one of claims 16 to 20 on a substrate, and
- Drying the resulting substrate to obtain said coated substrate.

26. The method of claim 25, wherein the depositing step is performed by a deposition technique selected from the **inkjet**, coating, screen printing, spraying, flexographic printing, **gravure printing** and offset.

27. A coated substrate obtainable by the process according to any one of claims 25 or 26.

28. battery electrode membrane fuel proton exchange comprising a coated substrate according to claim 27, said electrode being anodic or cathodic.

29. membrane fuel cell proton exchange comprising a coated substrate according to claim 27 or an electrode according to claim 28.

11.17. SULFONATED PERFLUOROSULFONIC ACID POLYELECTROLYTE MEMBRANES

Patent number: **WO2014118363A1**

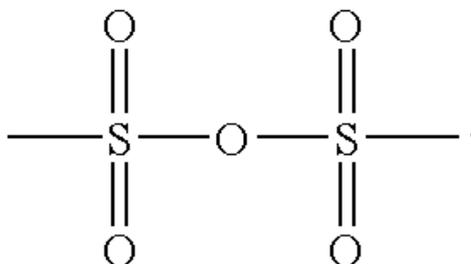
Priority date: 2005-08-05

ABSTRACT

New proton conducting membranes are made of perfluorosulfonic acid polymers films that have been treated by exposing them to a chlorosulfonating agent. The membranes are used as a proton exchange membrane in PEM fuel cells operating at temperatures above 95° C., or at low relative humidity. In various embodiments, the treated films have superior physical properties such as tensile strength, when compared to an untreated film. In some embodiments, the ion exchange capacity (IEC) of the treated films is increased.

CLAIMS (20)

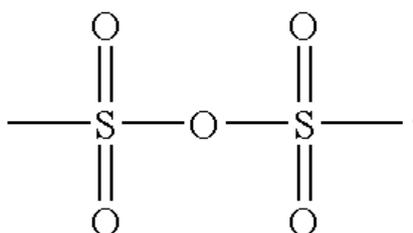
1. A solid polymer electrolyte made by a process comprising, reacting a perfluorosulfonic acid polymer film with a halosulfonating agent.
2. A solid polymer electrolyte according to claim 1, comprising crosslinks having structure



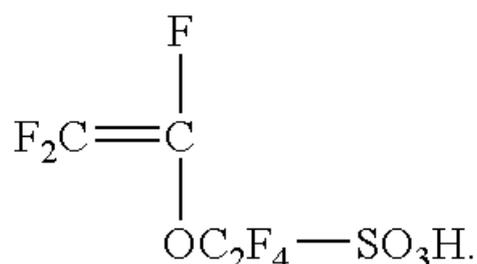
3. A solid polymer electrolyte according to claim 1, having an equivalent weight of 800 to 1200.
4. A solid polymer electrolyte according to claim 1, having an equivalent weight of 900 to 1000.
5. A solid polymer electrolyte according to claim 1, wherein the halosulfonating agent comprises chlorosulfonic acid.
6. An electrochemical device comprising a solid polymer electrolyte according to claim 1.
7. A proton exchange membrane comprising a solid polymer electrolyte according to claim 1.
8. A fuel cell comprising a proton exchange membrane according to claim 7.
9. A method for preparing a treated film suitable for use as a proton exchange membrane, comprising casting a film of a perfluorosulfonic acid polymer having an equivalent weight of 800 to 1200 onto a hard substrate;
floating the film off the substrate in a liquid;
exposing the film to a solution comprising a halosulfonating reagent; and
drying the exposed film after removing it from the solution.



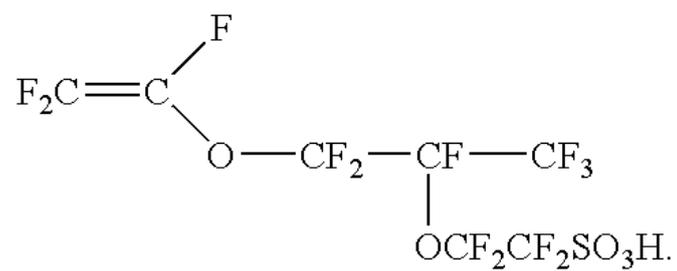
10. A method according to claim 9, wherein the perfluorosulfonic acid film has an equivalent weight of 800 to 1000.
11. A method according to claim 9, wherein the halosulfonating agent comprises chlorosulfonic acid.
12. A method according to claim 9, wherein drying comprises air drying.
13. A method according to claim 9, wherein casting comprises draw bar coating, **gravure coating**, or solution casting.
14. A fuel cell comprising, an anode; a cathode; a proton exchange membrane disposed between the anode and the cathode;
an inlet for hydrogen adjacent the anode; and
an inlet for oxygen adjacent the cathode,
wherein the proton exchange membrane comprises a PFSA film treated by exposure to a halosulfonating agent.
15. A fuel cell according to claim 14, wherein the proton exchange membrane comprises a polymer having an equivalent weight of 800 to 1200.
16. A fuel cell according to claim 15, wherein the equivalent weight is 900 to 1000.
17. A fuel cell according to claim 14, wherein the proton exchange membrane comprises sulfonic acid anhydride cross-links of structure



18. A fuel cell according to claim 14, wherein the perfluorosulfonic acid comprises a copolymer of tetrafluoroethylene and



19. A fuel cell according to claim 14, wherein the perfluorosulfonic acid comprises a copolymer of tetrafluoroethylene and



20. A fuel cell according to claim 14, wherein the halosulfonating agent comprises chlorosulfonic acid.



11.18. MULTILAYERED STRUCTURES AND METHODS FOR PRODUCING THE SAME

Patent number: **WO2004110599A2**

Priority date: 2003-05-27

ABSTRACT

The invention relates to methods for producing membranes, methods for producing membrane electrode units and membranes produced by these methods. The claimed membranes and membrane electrode units may be used to produce energy electrochemically or photochemically, in particular in membrane fuel cells (H₂ or direct methanol fuel cells) at temperatures from 20 to +180 °C. In one embodiment, working temperatures of up to 250 °C are possible. The claimed membranes and membrane electrode units can be used in membrane methods, in particular in galvanic cells, in secondary batteries, in electrolysis cells, in membrane separation processes such as gas separation, pervaporation, perstraction, reverse osmosis, electrodialysis, diffusion dialysis and for the separation of alkene-alkane mixtures or for the separation of mixtures of which one component forms complexes with silver ions.

CLAIMS

1. Use of dispersions suitable for the layered structure of a galvanic element, wherein the layers are applied in particular with only a manufacturing method and have different functional properties. Particularly advantageous methods of preparation are spraying, printing (for example screen printing, letterpress printing, **gravure printing**, pad printing, **inkjet printing**, stencil printing), doctor blade method, a CVD method, or lithographic process and transfer process. The functional properties of the layers can be present individually or in any combination and include ionic conductivity, electronic conductivity, mixed ionic and electronic conductivity, hydrophobic, hydrophilic, catalytic properties, and mechanical properties such as good adhesion, high tensile strength and appropriate thermal expansion. The layers may be formed porous or dense.
2. application of the mentioned under claim 1 dispersions on a porous carrier substrate, whose open porosity should be at least 50%, wherein the carrier substrate may not be conductive or both electronically conductive. A preferred embodiment includes a substrate having a smooth surface as possible, in particular, chemical stability to acids and organic solvents, thermal resistance preferably to max. 350 °C, a high mechanical stability, in particular with a bending stiffness of greater than 30 MPa and a modulus of elasticity greater than 9000 MPa,
3. Formation of porous layers having the specified under claim 1 dispersions by suitable manufacturing process or the addition of suitable pore formers.



11.19. COATING SLURRY FOR CATION-CONDUCTING POLYMER COMPOSITE MEMBRANE, METHOD FOR PRODUCING CATION-CONDUCTING POLYMER COMPOSITE MEMBRANE USING THE COATING SLURRY, MEMBRANE-ELECTRODE ASSEMBLY, AND FUEL CELL

Patent number: **WO2004110599A2**

Priority date: 2003-05-27

ABSTRACT

Disclosed herein is a slurry-type coating solution for cation-conducting polymer composite membranes that is capable of producing cation-conducting polymer composite membranes with high ionic conductivity as well as low methanol permeability and low ohmic resistance when used in direct-methanol fuel cells, via pluralization of solvents and use of specific additives. The coating slurry comprises about 1 to about 10 parts by weight of a sulfonated clay, about 100 parts by weight of a cation exchange group-containing polymer, and a co-solvent consisting of a high-boiling point solvent with a boiling point of about 180 to about 250° C. and a low-boiling point solvent with a boiling point of about 100 to about 180° C.

CLAIMS (19)

1. A coating slurry for a cation-conducting polymer composite membrane comprising: about 1 to about 10 parts by weight of a sulfonated clay; about 100 parts by weight of a cation exchange group-containing polymer; and a co-solvent comprising a high-boiling point solvent with a boiling point of about 180 to about 250° C. and a low-boiling point solvent with a boiling point of about 100 to about 180° C.
2. The coating slurry for a cation-conducting polymer composite membrane according to claim 1, wherein the high-boiling point solvent and the low-boiling point solvent are used in a weight ratio of about 1:20 to about 1:1.5.
3. The coating slurry for a cation-conducting polymer composite membrane according to claim 1, wherein the coating slurry has a viscosity of about 1,000 to about 5,000 cps.
4. The coating slurry for a cation-conducting polymer composite membrane according to claim 1, wherein the cation exchange group-containing polymer is selected from fluorine-based polymers comprising at least one side chain comprising at least one cation exchange group, hydrocarbon-based polymers comprising at least one side chain comprising at least one cation exchange group, and mixtures thereof.
5. The coating slurry for a cation-conducting polymer composite membrane according to claim 4, wherein the hydrocarbon-based polymer comprising at least one side chain comprising at least one cation exchange group is selected from polysulfone-based polymers, polyaryl ether sulfone-based polymers, polyphosphazene-based polymers, polyether ketone-based polymers, polyaryl ether ketone-based polymers, poly(phthalazinone ether ketone)-based polymers, polyimide-based polymers, polybenzimidazole-based polymers, acrylonitrile-butadiene-styrene (ABS)-based polymers, styrene-butadiene rubber (SBR)-based polymers, polystyrene-based polymers, polyolefin-based polymers, polycarbonate-based polymers, poly ethylene terephthalate (PET)-based polymers, poly ethylene naphthalate (PEN)-based polymers, acryl-based polymers and mixtures thereof.



6. The coating slurry for a cation-conducting polymer composite membrane according to claim 1, wherein the cation exchange group is at least one selected from a sulfonic acid group, a phosphonic acid group, a sulfuric acid group, a phosphoric acid group, a carboxylic acid group and a sulfonimide group.
7. The coating slurry for a cation-conducting polymer composite membrane according to claim 1, wherein the sulfonated clay comprises a sulfonic acid and comprises at least one clay selected from montmorillonite (MMT), illite, kaolinite, vermiculite, smectite, hectorite, mica, bentonite, nontronite, saponite, zeolite, alumina, rutile, talc, and mixtures thereof.
8. The coating slurry for a cation-conducting polymer composite membrane according to claim 1, wherein the high-boiling point solvent comprises at least one solvent selected from N-methyl-2-pyrrolidinone (NMP), dimethyl sulfoxide (DMSO), ethylene glycol (EG), and mixtures thereof.
9. The coating slurry for a cation-conducting polymer composite membrane according to claim 1, wherein the low-boiling point solvent comprises at least one solvent selected from N,N-dimethyl acetamide (DMAc), dimethylformamide (DMF), cyclopentanone, H₂O, and mixtures thereof.
10. The coating slurry for a cation-conducting polymer composite membrane according to claim 1, comprising a fluorine-based polymer comprising at least one side chain comprising at least one cation exchange group, sulfonated montmorillonite, and a co-solvent comprising NMP as a high-boiling point solvent and DMAc as a low-boiling point solvent.
11. A method for producing a cation-conducting polymer composite membrane comprising: coating a coating slurry comprising about 1 to about 10 parts by weight of a sulfonated clay; about 100 parts by weight of a cation exchange group-containing polymer; and a co-solvent comprising a high-boiling point solvent with a boiling point of about 180 to about 250° C. and a low-boiling point solvent with a boiling point of about 100 to about 180° C. on one side of a polymer film to form a coating film; subjecting the coating film to primary-drying to primarily remove the low-boiling point solvent in the coating film; and subjecting the coating film to secondary-drying to primarily remove the high-boiling point solvent in the coating film.
12. The method according to claim 11, wherein the coating step comprises doctor blade tape casting.
13. The method according to claim 11, wherein the polymer film is selected from poly(ethylene terephthalate) (PET)-based films, poly(ethylene naphthalate)(PEN)-based films, polycarbonate (PC)-based films, teflon-based films, polyimide-based films, polyolefin-based films, and films surface-treated with a release material.
14. The method according to claim 11, wherein the coating film has a thickness of about 10 μm to about 3 mm.
15. The method according to claim 11, wherein the coating film is produced with a coater selected from a die coater, comma coater, a blade coater and a **gravure coater**.
16. The method according to claim 11, further comprising:
rolling the coating film, after secondary-drying, wherein the overall process is carried out under the conditions that a length (m) of drying equipment/a line run rate (m/min) of the polymer film is about 2 to about 20.
17. A cation-conducting polymer composite membrane comprising: a film comprising sulfonated clay and a cation exchange group-containing polymer; and a polymer film, wherein the cation-conducting polymer composite membrane has an ionic conductivity of about 0.092 S/cm or higher and a methanol permeability of about 1.25 cm²/sec or lower.



18. A membrane-electrode assembly comprising: a cation-conducting polymer composite membrane produced by the method according to claim 11; catalyst layers each deposition-coated onto both sides of the cation-conducting polymer composite membrane; and gas diffusion layers each arranged on the catalyst layers.
19. A fuel cell comprising: a membrane-electrode assembly according to claim 18; and a pair of bipolar plates each arranged on both sides of the membrane-electrode assembly.



11.20. ELECTRODE WITH CATALYST SEGMENTATION

Patent number: **US9595720B2**

Priority date: 2013-03-14

ABSTRACT

A fuel cell assembly includes an anode with a catalyst layer and a gas inlet end, and a cathode with a catalyst layer and a gas inlet end. The assembly comprises a catalyst layer including a first and second set of catalyst segment pairs spaced apart respectively with first and second distances, a first ratio of an average segment width of the first set of catalyst segment pairs relative to the first distance being different from a second ratio of an average segment width of the second set of catalyst segment pairs relative to the second distance.

CLAIMS (28)

What is claimed is:

1. A fuel cell assembly including an anode and cathode, each comprising:
a catalyst layer including a plurality of pairs of catalyst segments disposed between an inlet end and an outlet end, a distance separating the segments of each of the pairs increasing from the inlet end to the outlet end.
2. The fuel cell assembly of claim 1, wherein the plurality of pairs of catalyst segments comprises a first pair of catalyst segments and a second pair of catalyst segments, and wherein the distance comprises a first distance separating individual segments of the first pair of catalyst segments and a second distance separating individual segments of the second pair of catalyst segments.
3. The fuel cell assembly of claim 2, wherein at least one of the first and second distances is no less than 200 micrometers.
4. The fuel cell assembly of claim 2, further comprising a third pair of catalyst segments located between the first and second pairs of catalyst segments, a third distance separating individual segments of the third pair of catalyst segments, the third distance being greater than the first distance and smaller than the second distance.
5. The fuel cell assembly of claim 2, further comprising a first spacing material positioned within the first distance and a second spacing material positioned within the second distance, wherein the first spacing material is less electrically conductive than the second spacing material.
6. The fuel cell assembly of claim 2, further comprising a first and second spacing material, each sized to allow for a gap of at least 0.2 mm on either side of the first or second spacing material.
7. The fuel cell assembly of claim 2, further comprising a first and second spacing material positioned between the first and second distances respectively, wherein the first and second spacing materials have a width between 0.2 and 2 mm.
8. The fuel cell assembly of claim 2, further comprising a first spacing material positioned within the first distance and a second spacing material positioned within the second distance wherein the first and second spacing materials are insulating materials selected from the group consisting of PTFE,



- PVDF, perfluorinated sulfonic acids, perfluorinated polymers, fluorocarbons and combinations thereof.
9. A fuel cell assembly including an anode and a cathode, each comprising: a catalyst layer including an inlet end and an outlet end; a first set of catalyst segment pairs located at the inlet end and a second set of catalyst segment pairs located at the outlet end, individual segments of the first and second sets of catalyst segment pairs are spaced apart respectively with first and second distances, and a first ratio of a first average segment width relative to the first distance being smaller than a second ratio of a second average segment width relative to the second distance.
 10. The fuel cell assembly of claim 9, wherein the first average segment width is smaller than the second average segment width.
 11. The fuel cell assembly of claim 9, wherein one or both of the first and second average segment width are no less than 100 micrometers.
 12. The fuel cell assembly of claim 9, wherein the first ratio is 2.5 to 12.5 and the second ratio is 10 to 50.
 13. The fuel cell assembly of claim 9, wherein the first set of catalyst segment pairs is positioned between the inlet end and the second set of catalyst segment pairs, wherein the first distance is smaller than the second distance.
 14. The fuel cell assembly of claim 9, further comprising a third set of catalyst segment pairs located between the first and second sets of catalyst segment pairs, individual segments of the third set of catalyst segment pairs being spaced apart with a third distance, the third set of catalyst segment pairs having a third average segment width, a third ratio of the third average segment width relative to the third distance being greater than the first ratio and smaller than the second ratio.
 15. The fuel cell assembly of claim 9, further comprising a third set of catalyst segment pairs separated with a third distance and a third spacing material positioned within the third distance, wherein the third spacing material is more electrically conductive than the first and second spacing materials.
 16. The fuel cell assembly of claim 15, wherein the third spacing material is an insulating material selected from the group consisting of PTFE, PVDF, perfluorinated polymers, fluorocarbons and combinations thereof.
 17. The fuel cell assembly of claim 9, further comprising a first spacing material being positioned within the first distance and a second spacing material being positioned within the second distance.
 18. The fuel cell assembly of claim 17, wherein the first spacing material is less electrically conductive than the second spacing material.
 19. The fuel cell assembly of claim 17, wherein the first spacing material comprises PTFE, PVDF, perfluorinated polymers, fluorocarbons, or a combination thereof.
 20. The fuel cell assembly of claim 17, wherein the first spacing material is less electrically conductive than the first set of catalyst segment pairs.
 21. The fuel cell assembly of claim 17 wherein the second spacing material is less electrically conductive than the second set of catalyst segment pairs.
 22. A method of improving the durability of a fuel cell having an anode and a cathode, with an inlet and an outlet, comprising the step of: reducing in-plane transfer of electrons within the anode by providing a catalyst layer for both the anode and cathode with a plurality of pairs of catalyst



segments disposed between an inlet end and an outlet end, a distance separating the segments of each of the pairs increasing from the inlet end to the outlet end.

23. The method of claim 22, wherein the catalyst segments are created using a **gravure technique**.
24. The method of claim 22, wherein the catalyst segments are created using **inkjet printing**.
25. The method of claim 22, further comprising a step of depositing a material selected from the group consisting of PTFE, PVDF, perfluorinated sulfonic acids, perfluorinated polymers, fluorocarbons and combinations thereof in between the catalyst segments.
26. The method of claim 22, wherein a greater number of the catalyst segments are placed in proximity of the inlet end than the outlet end.
27. The method of claim 22, further comprising a step of minimizing loss of a catalyst active area and mechanical integrity by limiting a number of the catalyst segments.
28. A method of improving a hydrogen fuel cell having an anode and a cathode, comprising the step of: creating a predefined hydrogen/air front on the cathode to enable lower half-cell potentials and higher surface area, wherein each anode and cathode comprises a catalyst layer including a plurality of pairs of catalyst segments disposed between an inlet end and an outlet end, a distance separating the segments of each of the pairs increasing from the inlet end to the outlet end.



11.21. METHOD FOR THE PREPARATION OF CATALYST-COATED MEMBRANES

Patent number: **EP2774203B1**

Priority date: 2011-11-04

ABSTRACT

The present invention is directed to a method for the preparation of catalyst-coated membranes for use in electrochemical cells, more specifically to the manufacture of integral catalyst-coated membranes for use in PEM (polymer-electrolyte-membrane) fuel cells. The process comprises the application of a coating dispersion containing an ion exchange resin (ionomer) onto a catalyst layer applied to a supporting substrate. According to the invention, the ionomer dispersion is characterized by a low viscosity and a high ionomer concentration.

CLAIMS (24)

Method for preparing a 3-layer catalyst-coated membrane (CCM) comprising a first catalyst layer, an ionomer membrane and a second catalyst layer, said method comprising the steps of

- a) preparing a first catalyst layer on a supporting substrate,
- b) coating the first catalyst layer with an ionomer dispersion to form an ionomer membrane in contact with the first catalyst layer,
- c) applying the second catalyst layer on top of the ionomer membrane,

wherein the ionomer dispersion applied in step b) has a viscosity in the range of 0,01 to 0,4 Pa.s (10 to 400 centipoise), measured at 25 °C and a shear rate of 100 s⁻¹, and an ionomer concentration in the range of 15 to 35 wt.-%.

Method according to claim 1, wherein in step a) the first catalyst layer is prepared by a coating process using a catalyst ink, by a vacuum deposition process or by combinations thereof.

Method according to claim 1 or 2, wherein in step c) the second catalyst layer is applied by a coating process using a catalyst ink.

Method according to claim 1 or 2, wherein in step c) the second catalyst layer is applied by a decal transfer process transferring a prefabricated catalyst layer on top of the ionomer membrane using heat and pressure.

Method according to claim 4, wherein in said decal transfer process the prefabricated catalyst layer is prepared by a coating process using a catalyst ink, by a vacuum deposition process or by combinations thereof

Method according to any one of claims 1 to 5, further comprising the step of

- d) annealing the layer structure at temperatures of at least 120°C after step b) and/or step c).

Method according to any one of claims 1 to 6, further comprising additional drying steps at least after step a) and b), using drying temperatures in the range of 40 to 120°C.

Method according to any one of claims 1 to 7, wherein the ionomer membrane is a cast membrane, comprising predominantly ionomer.



Method according to any one of claims 1 to 8, wherein the ionomer membrane is a reinforced membrane, comprising a microporous reinforcement film.

Method according to claim 9, wherein the microporous reinforcement film comprises expanded PTFE.

Method according to any one of claims 1 to 10, wherein the ionomer dispersion comprises fully or partially fluorinated polymers.

Method according to claim 11, wherein the fully or partially fluorinated polymers contain functional groups selected from sulfonic (-SO₃H), carboxylic (-COOH), phosphonic (-PO₃H₂), sulfonyl amide (-SO₂NH₂), bis-sulfonyl imide (-SO₂NHSO₂-), bis-carbonyl imide (-CONHCO-) and sulfonyl carbonyl imide (-SO₂NHCO-) groups and mixtures and combinations thereof.

Method according to any one of claims 1 to 12, wherein the ionomer dispersion comprises water and at least one polar organic solvent with a dielectric constant ≥ 15 .

Method according to any one of claims 1 to 13, wherein the catalyst layers comprise platinum-group based electro-catalysts.

Method according to any one of claims 1 to 14, wherein the catalyst layers are applied by casting or printing inks by methods selected from the group of knife coating, slot-die coating, slide coating, curtain coating, roll coating, screen printing, ink-jet printing, **gravure printing** and flexographic printing and combinations thereof.

Method according to any one of claims 1 to 15, wherein the first catalyst layer applied in step a) is the cathode layer.

Method according to any one of claims 1 to 16, further comprising the step of removing the supporting substrate from the first catalyst layer of the CCM assembly.

Method according to any one of claims 1 to 17, wherein the supporting substrate for applying the first catalyst layer in step a) is an inert polymer film or paper film.

Method according to any one of claims 1 to 16, wherein the supporting substrate is a gas diffusion layer.

Method according to any one of claims 1 to 19, wherein the supporting substrate is coated with a microporous layer comprising carbon black and a hydrophobic binder prior to preparing the first catalyst layer.

Method according to any one of claims 1 to 20, fully or partially carried out on a continuous manufacturing line.

Method according to claim 1, wherein the ionomer dispersion applied in step b) has a viscosity in the range of 10 to 80 centipoise (cP).

Catalyst-coated membrane (CCM), obtainable by the method according to any one of claims 1 to 22, wherein the apparent cathode catalyst layer resistivity ρ_a is less than 650 Ωcm (measured at 85°C and 21% relative humidity).

Catalyst-coated membrane (CCM), obtainable by the method according to any one of claims 1 to 22, wherein the apparent cathode catalyst layer resistance r_{LN} (normalized to the precious metal loading) is in the range of 0.1 $\Omega\text{cm}^4\text{mg}^{-1}$ to 1.5 $\Omega\text{cm}^4\text{mg}^{-1}$ (measured at 85°C and 21% relative humidity).



11.22. MEMBRANE ELECTRODE ASSEMBLY MANUFACTURING PROCESS

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ABSTRACT

A method of making a component of a membrane electrode assembly comprising the steps of forming an electrode on an air-permeable backer comprising ePTFE, depositing a mixture comprising ionomer and a water-insoluble alcohol onto said electrode, drying said mixture to form a protective ionomer layer, and depositing an ePTFE-reinforced ionomer layer onto said protective ionomer layer.

CLAIMS (35)

What is claimed is:

1. A method of making a component for a membrane electrode assembly comprising the steps of:
 - (a) providing an air-permeable backer;
 - (b) depositing an electrode onto said backer;
 - (c) depositing an aqueous wet layer comprising a fluoroionomer mixture onto said electrode; and
 - (d) substantially drying said wet layer to form a protective ionomer layer.
2. A method as defined in claim 1 wherein an air-permeable backer comprises an expanded polymer having release characteristics.
3. A method as defined in claim 2 wherein the expanded polymer is ePTFE.
4. A method as defined in claim 3 wherein said expanded polymer has a mass per area of less than about 16 g/m² of ePTFE.
5. A method as defined in claim 3 wherein said expanded polymer has a bubble point of greater than about 70 psi PMI.
6. A method as defined in claim 3 wherein said air-permeable backer has a Z-strength sufficient to prevent cohesive failure of said ePTFE when said electrode is peeled off of said air-permeable backer.
7. A method as defined in claim 1 wherein an air-permeable backer is a gas diffusion layer.
8. A method as defined in claim 1 further comprising coupling a fabric to said backer.
9. A method as defined in claim 8 wherein said air-permeable backer is dimensionally stable within +/-4% throughout the manufacturing process.
10. A method as defined in claim 8 wherein said fabric comprises polyester.
11. A method as defined in claim 8 wherein said fabric has a thickness of less than about 0.006 inches.
12. A method as defined in claim 8 wherein said fabric has a mass/area of less than about 64 g/yd².
13. A method as defined in claim 8 further comprising the step of bonding said fabric to said backer with an adhesive in a discontinuous pattern.



14. A method as defined in claim 13 wherein said fabric is dot-laminated to said backer with a urethane adhesive.
15. A method as defined in claim 13 wherein said adhesive is a solvent-stable adhesive.
16. A method as defined in claim 1 wherein said wet layer comprises a water-insoluble alcohol and ionomer.
17. A method as defined in claim 16 wherein said ionomer is perfluorosulfonic acid (PFSA) ionomer.
18. A method as defined in claim 16 wherein said wet layer is aqueous and comprises greater than about 60 wt % water.
19. A method as defined in claim 16 wherein said wet layer is aqueous and comprises greater than about 90 wt % water.
20. A method as defined in claim 16 wherein said wet layer is aqueous and comprises less than about 3 wt % of said insoluble alcohol.
21. A method as defined in claim 16 wherein said wet layer is aqueous and comprises less than about 5 wt % of said insoluble alcohol.
22. A method as defined in claim 16 wherein said water-insoluble alcohol comprises hexanol.
23. A method as defined in claim 16 wherein said wet layer further comprises a water-soluble alcohol.
24. A method as defined in claim 23 wherein said wet layer comprises less than about 10 wt % of said water-soluble alcohol.
25. A method as defined in claim 23 wherein said water-soluble alcohol comprises glycol ether present in an amount of less than about 5 wt %.
26. A method as defined in claim 1 further comprising a step (e) depositing a proton conducting layer onto said protective ionomer layer.
27. A method as defined in claim 26 wherein said proton conducting layer comprises an ionomer.
28. A method as defined in claim 26 wherein said proton conducting layer comprises a reinforcement.
29. A method as defined in claim 28 wherein said reinforcement comprises an ePTFE membrane.
30. A method as defined in claim 26 further comprising the step of depositing an ionomer layer onto said proton conducting layer.
31. A method as defined in claim 26 further comprising the step of depositing another electrode onto said proton conducting layer.
32. A method as defined in claim 30 further comprising the step of depositing another electrode onto said ionomer layer.
33. A method as defined in claim 1 wherein said protective ionomer layer has a thickness of about 0.1 to about 25 microns.
34. A method as defined in claim 1 wherein said protective ionomer layer has a thickness of about 0.1 to about 10 microns.
35. A method as defined in claim 1 wherein said protective ionomer layer has a thickness of about 0.1 to about 3 microns.

APPENDIX:

| Operation | Shear Rate (s^{-1}) |
|-----------------------------|-------------------------|
| Coating | |
| Dip | 10–100 |
| Roll, reverse | 1,000–100,000 |
| Roll, forward | 10–1,000 |
| Spray | 1,000–10,000 |
| Slide | 3,000–120,000 |
| Gravure, reverse | 40,000–1,000,000 |
| Gravure, forward | 10–1,000 |
| Slot die | 3,000–100,000 |
| Curtain | 10,000–1,000,000 |
| Blade | 20–40,000 |
| Ancillary operations | |
| Simple mixing | 10–100 |
| High shear mixer | 1,000–100,000 |
| Measurement | |
| Brookfield | 1–300 |
| ICI | 10,000 |
| Haake | 1–20,000 |
| Fenske-Cannon | 1–100 |

Figure a. Comparison of rheological properties for various coating and printing methods [83]

| Method | Tolerant to thickness variations | Cockle tolerant | Buckle tolerant | Low shear viscosity (cP) | No. of layers | Wet thickness (μm) | Coating accuracy | Max. speed(m/min) | Intermittent/patterned |
|--------------------|----------------------------------|-----------------|-----------------|--------------------------|---------------|---------------------------|------------------|-------------------|------------------------|
| Mayer rod | Yes | Marginal | No | 20–1,000 | 1 | 5–50 | Moderate | 250 | No |
| Dip | Yes | Ok | Yes | 20–1,000 | 1 | 5–100 | Precision | 150 | No |
| Air knife | Yes | Ok | Marginal | 5–500 | 1 | 2–40 | Good | 500 | No |
| Forward roll | No | No | Marginal | 20–1,000 | 1 | 10–200 | Moderate | 150 | No |
| Reverse roll | Yes | Marginal | No | 100–50,000 | 1 | 5–400 | Precision | 400 | No |
| Knife over roll | No | No | Marginal | 100–50,000 | 1 | 25–750 | Moderate | 150 | No |
| Knife over blanket | Marginal | No | No | 100–50,000 | 1 | 25–750 | Moderate | 150 | No |
| Flexible blade | Yes | No | No | 500–40,000 | 1 | 25–750 | Good | 1500 | No |
| Slot | Yes | Marginal | Marginal | 5–20,000 | 1–3 | 15–250 | Precision | 500 | Ok for patches |
| Extrusion | Yes | Marginal | Marginal | 50,000–5,000,000 | 1–15 | 15–1000 | Good | 700 | No |
| Slide | Yes | Marginal | Marginal | 5–500 | 1–18 | 15–250 | Precision | 200 | No |
| Curtain | Yes | Yes | Yes | 5–500 | 1–18 | 2–500 | Precision | 400 | No |
| Gravure, direct | Yes | Ok | No | 1–5,000 | 1 | 1–25 | Good | 700 | Excellent |
| Gravure, offset | Yes | Ok | No | 100–50,000 | 1 | 1–400 | Good | 300 | Flexography |

Figure b. Extended comparison of technical aspects for coating and printing technologies [85]



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