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(54) Title: GAS DIFFUSION ELECTRODE

(57) Abstract: A gas diffusion electrode and process of manufacture comprising a gas diffusion layer with a surface to which platinum nanowires have been applied; wherein the surface is at least partially weakly hydrophobic or hydrophilic, forming a weakly hydrophobic and/or hydrophilic surface or weakly hydrophobic and/or hydrophilic regions on the surface.



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Gas Diffusion Electrode

Field

[0001] The invention relates to a gas diffusion electrode (GDE), in particular to a gas diffusion electrode comprising an integral catalyst surface on a gas diffusion layer (GDL) and to processes for making the GDL. GDEs including the GDL, and fuel cells including the GDE are also protected.

Background

[0002] Fuel cells have potential for stationary and portable power applications in electric vehicles, buildings and other portable power generators. Low temperature fuel cells, usually refer to polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs), employing solid protonic electrolyte, utilizing hydrogen or liquid fuels to deliver continuous power, have higher utilization efficiencies and intrinsically low polluting emissions comparing with conventional energy generators (e.g. Internal combustion engines). However, the commercial viability of low temperature fuel cells for power generation depends upon solving a number of manufacturing, cost, and durability problems, especially the hinder associated with the catalyst electrodes where the electrochemical reactions happen and the power generates.

[0003] The conventional method for the fabrication of the catalyst electrode is usually a 3-step process.

At first the catalyst (e.g. platinum (Pt)) precursor is reduced to synthesize catalyst nanoparticles, and this usually occurs at a high temperature. Depending on the catalyst type, support materials such as carbon black may be needed. If control of the catalyst shape is needed, surfactants are usually required. If this is done by polyol process, then organic solvents are often necessary.

Then the catalyst nanoparticles are mixed with electrolyte ionomer and organic solvents to make a catalyst ink.

Finally, the catalyst ink is coated onto gas diffusion layer (GDL) or electrolyte membrane surface to fabricate a catalyst electrode.

[0004] Methods have been developed to prepare catalysts, such as formic acid which can be used as the reducing agent to synthesize Platinum nanowires in aqueous solution at room temperature, making the first step much easier. However, this 3-step method is still

very complex because every parameter in each step can change the final electrode performance.

[0005] A GDE with in-situ grown Platinum nanowire arrays on GDL surface has been proposed by Shangfeng Du (A facile route for polymer electrolyte membrane fuel cell electrodes with in situ grown platinum nanowires; Journal of Power Sources; Volume 195, Issue 1, 2010, pages 289-292). The simple fabrication process and good catalytic performance result in a low cost GDE which can provide reducing the cost of fuel cells. However, it has been found that the superhydrophobic (water contact angles greater than 150°) or highly hydrophobic (water contact angles greater than 130°) nature of the GDL surface described causes the Platinum nanowires to grow mainly at the edges and corners of the GDL surface, leading to a non-uniform catalyst layer thus relatively poor fuel cell performance. Innovative solutions for common problems are urgently needed in practical applications.

[0006] Fuel cells contain GDLs in order to allow gas to uniformly diffuse to the triple-phase boundary (TPB) in the catalyst layer, enabling the reaction gases (for instance hydrogen and oxygen) to contact with the catalyst and electrolyte thereby facilitating the fuel cell reaction. The most commonly used GDL materials are Teflon treated carbon paper or carbon cloth covered with a porous layer that contains carbon black spheres and Teflon. These materials are usually hydrophobic in order to remove water from the fuel cell and so prevent the fuel cell from flooding. But, the highly hydrophobic feature of the GDL surface makes it difficult to use the surface as a direct support for depositing electrocatalysts in aqueous systems, which finally results in an non-uniform Platinum nanowire distribution on the GDL surface as mentioned above. There is therefore a need for a GDL which can provide good fuel cell performance, and preferably an integral catalyst surface. The invention is intended to overcome or ameliorate at least some aspects of this problem.

Summary

[0007] Accordingly, in a first aspect of the invention there is provided a GDE comprising a GDL with a surface to which platinum nanowires have been applied; wherein the surface is at least partially hydrophobic or hydrophilic, forming a weakly hydrophobic surface or hydrophilic regions on the surface of the GDL.

[0008] The provision of a GDL that is surface coated (wholly or partially) with Platinum nanowires, often in the form of arrays, provides for the production of an integrated GDE.

[0009] The presence of a surface which is weakly hydrophobic, or even hydrophilic, provides a system where the GDL surface can be used as a direct support for the electrocatalyst. This is at least partly due to the change in hydrophobicity of the surface allowing, for the first time, the controlled, reliable deposition of Platinum nanowires so that these can form uniform arrays.

[0010] It could be said that the platinum nanowires or nanowire arrays form a catalyst layer on the GDL surface, the layer (or coating) being total, effectively total or partial on the GDL surface. As used herein, total coverage would be 100%; effectively total in the range 80 - 99.9% or 95 - 99.5% of the surface area covered or coated; and partial being in the range 30 - 95% of the surface, often 50 - 95% or 70 - 80% of the surface being coated with the platinum nanowire arrays.

[0011] As used herein the term "hydrophilic surface" is intended to mean a surface with a water contact angle of less than 90° (perhaps in the range 1-90°, 15-85°, or 30-60°) and the term "hydrophobic surface" is intended to mean a surface with a water contact angle of greater than 90° (perhaps in the range 90-179°, 95-150°, or 105-130°). The term "weakly hydrophobic surface" is intended to mean a surface with a water contact angle between 90-130° (perhaps in the range 90-120° or 90-105°); the term "highly hydrophobic surface" means a surface with a water contact angle in the range of 130-150°; and the term "superhydrophobic surface" means a surface with a water contact angle greater than 150° (perhaps in the range 150-175° or 155-165°). Whereas the term "highly hydrophilic surface" means a surface with a water contact angle in the range of 30-60°; and the term "weakly hydrophilic surface" means a surface with a water contact angle between 60-90°, often 75-90°. In addition, reference to a weakly hydrophobic/hydrophilic surface, or region is intended to include surfaces/regions which are weakly hydrophobic, hydrophilic and combinations thereof.

[0012] With regard to the percentage of the GDL surface which is either weakly hydrophobic or hydrophilic, this surface may be entirely or substantially entirely hydrophilic/weakly hydrophobic (for instance, wherein the surface has a surface area which is greater than 95% hydrophilic/weakly hydrophobic, greater than 97%, 98%, or 99% hydrophilic/weakly hydrophobic. In some cases, the surface may be greater than

99.5% hydrophilic/weakly hydrophobic. Often the surface will be 100% hydrophilic/weakly hydrophobic, or slightly less than 100% hydrophilic/weakly hydrophobic, such as 99.9% or less, 99.8% or less or 99.5% or less). Where the surface is less than 95% hydrophilic/weakly hydrophobic, we will refer to it herein as being a surface including hydrophilic/weakly hydrophobic regions on the surface. The hydrophilic/weakly hydrophobic regions will often form in the range 50 - 95% of the surface, often 60 - 85%, or 70 - 80% of the surface. The surface itself will often have a surface area which is in the range 50 - 100% hydrophilic/weakly hydrophobic, or 60 - 90%, or 70 - 80% hydrophilic/weakly hydrophobic.

[0013] The presence of a hydrophilic/weakly hydrophobic surface (or of hydrophilic/weakly hydrophobic regions on the surface) provides for a more uniform growth of platinum nanowires across the surface than has been possible before. The two factors of increased coverage and uniform distribution of the catalyst nanowires independently allow for the provision of a much larger electrochemical surface area (ECSA), thus a better fuel cell performance. In turn, the provision of this more hydrophilic surface enables a low catalyst loading in the GDE, reducing production costs and improving reliability.

[0014] It will often be the case that the platinum nanowires substantially cover the hydrophilic/weakly hydrophobic surface or hydrophilic/weakly hydrophobic regions on the surface of the GDL, as this is where the reaction solution can reach and form nucleus of catalyst metal and finally grow to single-crystal nanowire. Often the platinum nanowires will cover in the range 50 - 99% of the surface area of hydrophilic surface or hydrophilic regions on the surface, often 85 - 95%, or 90 - 95% of the hydrophilic/weakly hydrophobic surface or hydrophilic/weakly hydrophobic regions on the surface.

[0015] The GDL substrate may be selected from any of the many substrates are usually used in fuel cells, although often the substrate will be a substrate used in low temperature fuel cells such as carbon cloth, carbon paper or carbon paper with a porous layer. The carbon paper and carbon cloth may be woven or non-woven and may be coated, for instance with Teflon™. The substrate/GDL may have a porous layer. Where present the porous layer may be a layer between the catalyst layer and GDL support in the GDE. The presence of a porous layer allows uniform diffusion of the gaseous reaction media to the catalyst, whilst supporting the catalyst layer where necessary.

[0016] The platinum nanowires are typically of length in the range 50 - 500 nm, and/or of diameter in the range 1 - 10 nm. This allows the preparation of a remarkably thin catalyst layer, of thickness less than 1 μm . The thickness of the catalyst layer may be in the range 50 nm - 1 μm , often 100 - 500 nm, or 300 - 400 nm. Often the length of the nanowires will be in the range 100 - 400 nm, or 200 - 300 nm. Often the diameter of the nanowires will be in the range 1 - 10 nm, often 2 - 6 nm, allowing dense packing of nanowires across the hydrophilic/weakly hydrophobic surface or hydrophilic/weakly hydrophobic regions on the surface.

[0017] Such a thin catalyst layer can be achieved as the catalyst layer is typically constructed from a monolayer of platinum nanowire arrays. This novel structure significantly reduces the mass transfer resistance relative to conventional GDEs that usually have a catalyst layer with a thickness about 10 μm . The application of platinum nanowires to the hydrophilic/weakly hydrophobic surface to form the GDE provides a GDE with a much improved catalytic performance towards oxygen reduction reaction (ORR) in low temperature fuel cells, e.g. PEMFCs and DMFCs, than has previously been observed.

[0018] The physical dimensions of the GDL/GDE are not particularly limited, the simplicity of the GDE ensures that it is easy to prepare regardless of the product size, providing flexibility not previously available. As such, the GDE may be of thickness similar to known GDE's, for instance in the range 10 - 500 μm , with the resulting GDE being of active area in the range 1 mm^2 - 1 m^2 as necessary for the application. Plasma treatment is possible across this wide range of sizes.

[0019] As noted above, in the GDEs of the invention the platinum nanowires act as catalysts, and can do so effectively as the presence of the hydrophilic/weakly hydrophobic surface or hydrophilic/weakly hydrophobic regions on the surface promote a uniform distribution of nanowires in catalyst layer, resulting in good, reliable catalytic activity of the GDE.

[0020] In a second aspect of the invention, there is provided a membrane electrode assembly (MEA) for fuel cell comprising the GDE of the first aspect of the invention. Often the fuel cell will be a low temperature fuel cell such as a DMFC or a PEMFC. The incorporation of the GDE of the invention into such fuel cells reduces production costs and improves the reliability of the fuel cell as there are fewer components present to foul.

[0021] In a third aspect of the invention there is provided a process for making a GDE comprising the steps of:

- a. plasma treating a surface of a GDL; and
- b. applying platinum nanowires to the plasma treated surface.

5 [0022] Treatment of the surface with plasma converts highly/superhydrophobic end groups to weakly hydrophobic or even hydrophilic end groups, creating more nucleation sites and enabling the application of the platinum nanowires. In effect, the plasma treatment enhances the wettability of the GDL, allowing for the application of the platinum nanowires to the surface in sufficient quantities, and with a sufficiently even distribution,
10 to give a high catalytic activity to a GDE.

[0023] The GDL, and hence also the GDE, are very easy to construct, as the plasma techniques and platinum nanowire deposition process used are very simple, and hence easily to scale up. The GDE can be prepared using a single step from the plasma treated GDL, which can be conducted at room temperature. In comparison, known processes for
15 preparing GDEs, require (in addition to the provision of a GDL), the steps of making a catalyst ink and coating to fabricate the catalyst layer. These steps are not needed with the products of the invention, removing two of the three production steps for GDEs.

[0024] The process of the invention is a green and clean chemical process because there is no waste, and because (despite the use of nanowires in the GDE construction), the whole
20 procedure does not at any point generate free (potentially toxic) nanoparticles.

[0025] In some examples, the platinum nanowires are applied to the plasma treated surface by being grown onto the plasma treated surface. A wide variety of techniques may be used, as would be known to the person skilled in the art, although it will often be the case that the technique used will be selected from physical vapour deposition, chemical
25 vapour deposition, chemical reduction deposition, or combinations thereof.

[0026] Where a reduction process is used, the platinum-containing precursor will often be reduced on the plasma treated surface of the GDL. The platinum-containing precursor need only be such that it can be reduced to platinum under relatively mild conditions, without inhibiting the nanowire growth process or fouling the GDL. Often, the platinum-
30 containing precursor is selected from chloroplatinic acid (hexa)hydrate, platinic acid, sodium platinic chloride, potassium hexachloroplatinate, and combinations thereof.

[0027] Weak reducing agents are often used, to ensure that the GDL is not damaged, and that the nanowire growth process not prevented in any way. Often the reducing agent will be selected from hydrogen, formic acid, ascorbic acid, citric acid and combinations thereof.

5 [0028] Often the reduction of the platinum-containing precursor occurs in aqueous solution, avoiding the need to use potentially harmful organic solvents. Low temperatures may also be used, often in the range 5 - 50°C, often in the range 15 - 30°C or 20 - 25°C, (i.e. at or near to ambient temperature).

[0029] Using this method, platinum nanowire growth can be achieved at room
10 temperature, without using organic solvents, template, or inducing growth catalysts, which are usually necessary in fabricating conventional catalyst electrodes in fuel cells.

[0030] Alternatively conventional vapour deposition techniques may be used, these include physical and chemical vapour deposition and would be well known to the skilled reader. Such techniques can be advantageous in that the nanowire growth is easy to
15 control and so an evenly distributed catalyst layer will be produced; however, as such techniques are more complex than chemical reduction methods, often reduction techniques will be used in the subject invention.

[0031] The plasma treatment can be completed in a conventional plasma furnace, and active-screen furnaces are often used. The plasma gas may be hydrogen carried in an inert
20 gas, such as argon or nitrogen, of which often nitrogen will be used. Where the plasma gas is a combination of hydrogen and nitrogen, typically there will be more hydrogen than nitrogen, and so often the ratio will be 1:1 hydrogen:nitrogen or greater. Often the ratio will be in the range 2:1 - 5:1, often around 3:1 hydrogen:nitrogen.

[0032] For the purposes of the invention, plasma treatment will generally be at a
25 relatively low temperature, for instance in the range 50 - 250°C, often 75 - 200°C, often around 100°C, so in the range 80 - 120 °C or 90 - 110°C. This is advantageous as only minimal energy is consumed during the plasma treatment process. In addition, the duration of treatment can be short, for instance less than 2 hours, often less than 1 hour, less 30 minutes, often around 15 minutes. A range of 5 - 120 minutes would be typical,
30 with upper limits as above.

[0033] Unless otherwise stated each of the integers described in the invention may be used in combination with any other integer as would be understood by the person skilled in

the art. Further, although all aspects of the invention preferably “comprise” the features described in relation to that aspect, it is specifically envisaged that they may “consist” or “consist essentially” of those features outlined in the claims.

[0034] Further, in the discussion of the invention, unless stated to the contrary, the disclosure of alternative values for the upper or lower limit of the permitted range of a parameter, is to be construed as an implied statement that each intermediate value of said parameter, lying between the smaller and greater of the alternatives, is itself also disclosed as a possible value for the parameter.

[0035] In addition, unless otherwise stated, all numerical values appearing in this application are to be understood as being modified by the term “about”.

Brief Description of the Drawings

[0036] In order that the present invention may be more readily understood, it will be described further with reference to the figures and to the specific examples hereinafter.

[0037] Figures 1a and 1b show SEM images of GDEs with in-situ grown single crystal platinum nanowire arrays on un-treated (a) and plasma treated (b) Sigracet® GDL 35BC carbon paper (Thickness: 325 ± 25 microns; Area Weight: 110 ± 10 g/m²; Air permeability: 1.50 ± 1.00 cm³/(cm²·s); Electrical resistivity (TP): < 15 milliohms cm²);

[0038] Figures 2a and 2b show a comparison of the water contact angles for Sigracet® GDL 35BC before (a) and after (b) plasma treatment;

[0039] Figure 3 shows I-V and P-V of single DMFCs with a range of cathodes, including Johnson-Matthey DMFC cathode (Alfa Catalog Number: 045375; Non-woven carbon fibres: 60 wt%; Catalyst: 25 wt%; Carbon Black: 5 wt%; PTFE: 5 wt%; PFSA ionomer: 5 wt%) (■), a GDE with platinum nanowire array on un-treated carbon paper (●), and a GDE with platinum nanowire array on plasma treated carbon paper (▲). The platinum loadings are 4 mg cm⁻² (Johnson-Matthey), 4 mg cm⁻² (platinum nanowire GDEs on untreated carbon paper) and 2 mg cm⁻² (platinum nanowire GDEs on plasma treated carbon paper);

[0040] Figures 4a and 4b show a comparison of the water wetting angle for E-TEK® GDL 1200-W (Thickness: 275 microns; Basis weight: 200 g/m²; Air permeability: >8 cm³/(cm²·s); Electrical resistivity (TP): 410 milliohms-cm) before (a) and after (b) plasma treatment; and

[0041] Figure 5 shows I-V and P-V of single PEMFCs with cathodes of commercial *E-TEK*[®] GDE LT-120EW (Thickness: 310 microns; Basis weight: 180 g/m²; Air permeability: 40 cm³/(cm²·s); Electrical resistivity (TP): 685 milliohms-cm) (■), GDEs with platinum nanowire array on un-treated carbon cloth (●), and GDEs with platinum nanowire array on plasma treated carbon cloth (▲). The platinum loadings are 0.5 mg cm⁻² (E-TEK) and 0.4 mg cm⁻² (platinum nanowire GDEs).

Examples

10 **Example 1: DMFC cathode with single crystal platinum nanowire arrays grown on SIGRACET[®] GDL 35BC**

GDE preparation

[0042] A 5 cm² piece of SIGRACET[®] GDL 35BC carbon paper (GDL 35BC) was used as the GDL support to grow platinum nanowires.

[0043] At first, one piece of GDL 35BC was surface treated in an active-screen plasma furnace at 100°C for 15 minutes in a gas mixture of 75% H₂/25% N₂.

[0044] The procedure for the growth of single-crystal platinum nanowire arrays onto GDL surface was as follows: plasma treated or un-treated (plain) GDL 35BC carbon paper was sonicated for 10 minutes in formic acid (5 vol% aqueous solution), and then H₂PtCl₆ was added. To grow 4 mg cm⁻² platinum nanowires on GDLs, 53.12 mg H₂PtCl₆·6H₂O (20 mg Pt, 4 mg cm⁻² on GDL) was added into 32 mL aqueous solution containing 1.63 mL formic acid. The samples were stored at room temperature for 72 hours and while platinum nanowires were grown on the GDL surface. Then the carbon paper with platinum nanowire arrays was rinsed with deionised (DI) water 3 times, ethanol 3 times and DI water 3 times, followed by drying at 65°C for 24 hours.

[0045] SEM images of the platinum nanowire GDL with in-situ grown single crystal platinum nanowire arrays on un-treated (plain) and plasma treated GDL 35BC carbon paper are shown in Figures 1a and 1b. The carbon paper with in-situ grown platinum nanowires can be used directly as GDEs to fabricate membrane electrolyte assemblies (MEAs) for DMFCs.

[0046] As can be seen from a comparison of Figures 1a and 1b, the nanowire coating obtained where the surface is pretreated with plasma to improve the hydrophilicity is more uniform and more finely dispersed. This provides an improved catalytic surface. Evidence of the improved hydrophilicity of the plasma treated surface can be seen in Figures 2a and 2b, which show the water wetting angle for SIGRACET[®] GDL 35BC before and after plasma treatment. As can be seen Figure 2b, where the GDL has been plasma treated, the surface has a reduced wetting angle compared to Figure 2a.

Membrane Electrode Assembly (MEA) fabrication

[0047] The platinum nanowire GDEs with treated or un-treated GDL were assembled as cathodes with NAFION[®] NR-117 membranes (EW: 1100; Thickness: 183 microns; Basis weight: 360 g/m²; specific gravity: 1.97 g/cm³) to fabricate MEAs. The anodes were commercial Johnson Matthey DMFC anodes with catalyst loading of 4 mg PtRu cm⁻², onto which a thin NAFION[®] polymer ionomer layer was painted using a THF solution of NAFION[®] D1021 (Polymer content: 10-12 wt%; Water content: 87-90 wt%; VOC content: < 1 wt%; Specific gravity: 1.05-1.07 g/cm³) (volume ratio of NAFION[®] solution D1021 to THF = 1:2) followed by drying at room temperature for 30 minutes. The GDEs were then hot-pressed against the NAFION[®] NR-117 membrane at 140°C for 2 minutes under a constant pressure of 50 kg cm⁻². The comparative MEA was simultaneously fabricated with a NAFION[®] NR-117 membrane and commercial Johnson Matthey DMFC cathode (4 mg Pt cm⁻²) and anode used as both electrodes. Teflon[®] film with a thickness of 254 µm was used as gasket material in the DMFC hardware. The MEA was sandwiched between two stainless steel flow field plates to form a single cell with an active electrode area of 5 cm².

Single Cell Performance Test

[0048] The single cell test was performed at 75°C using an automatic fuel cell test system (EZstat-Pro, 1A, NuVant Systems Inc., USA). The anode was fed with 1 molL⁻¹ methanol at a flow rate of 1 mLmin⁻¹ without back pressure. The cathode was fed with non-humidified air at a flow rate of 100 standard cubic centimeters per minute (sccm) without back pressure. Before the test, the cell was conditioned with nanopure water at the anode and air at the cathode at 75°C. After conditioning, nanopure water was replaced

with aqueous methanol for 24h in galvanostatic mode at 10 mA cm^{-2} . Then the cell voltage was looped between 0.2 and 0.7 V at 5 mVs^{-1} for 5 cycles, and the fifth cycle was recorded.

[0049] The polarization and power density curves for three MEAs are shown in Figure 3.

- 5 As can be seen, the plasma treated platinum nanowire array performs better than both the commercial (Johnson-Matthey) and untreated systems - clearly showing the benefits of the invention.

Example 2: PEMFC cathode with single crystal platinum nanowire arrays grown on E-TEK[®] GDL 1200-W

GDE Preparation

- [0050] A $4 \times 4 \text{ cm}^2$ piece of E-TEK[®] GDL 1200-W carbon cloth was used as a GDL substrate to grow platinum nanowires. All other details are the same as in Example 1, except the amounts of chemicals used, which were as follows. To grow 0.4 mg cm^{-2} platinum nanowires on GDLs, 16.99 mg $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (6.4 mg Pt, 0.4 mg cm^{-2} on GDL) was added into 10.6 mL aqueous solution containing 0.53 mL formic acid.

- [0051] The water wetting angle comparison for E-TEK[®] GDL 1200-W before and after plasma treatment is shown in Figures 4a and 4b. As can be seen, the wetting angle is significantly reduced after plasma treatment, indicating a much increased hydrophilicity on the GDL surface, and hence an improved ability to accept the application of platinum nanowires.

MEA Fabrication

- 25 [0052] The procedure was the same as in Example 1, except that the materials used were as follows: A Nafion[®] 212 membrane (EW: 1100; Thickness: 50.8 microns; Basis weight: 100 g/m^2 ; specific gravity: 1.97 g/cm^3) is used to fabricate the MEAs, while the anodes are commercial E-TEK[®] GDE LT-120EW GDEs with a platinum loading 0.5 mg cm^{-2} . A comparison of the MEA of this example (i.e. with a NAFION[®] NR-212 membrane), and those with a commercial electrode (an E-TEK[®] GDE LT 120EW (Pt loading 0.5 mg cm^{-2})) as both electrodes, was made.

Single Cell Test

[0053] The MEAs were tested in a 16 cm²-PEMFC single cell hardware at a temperature of 70°C, using pure H₂ and air gases at 50% relative humidity (RH) and gas flows in the range of 120 and 300 mLmin⁻¹ with stoichiometries of 1.5(H₂)/2.0(Air) respectively. The back pressure of the humidified H₂ and air (identical at the anode and cathode sides) was 0.15 MPa. Measurements were controlled and recorded by a Bio-logic FCT-50S PEMFC test station (PaxiTech). The MEA was conditioned by break-in at 0.6 V for 12 hours, and thereafter the polarization curves were recorded at a scan rate of 1 mV s⁻¹. The polarization and power density curves for three MEAs are shown in Figure 5. As can be seen, the plasma treated platinum nanowire array outperforms both current commercial systems (*E-TEK*[®]), and the untreated systems.

[0054] It should be appreciated that the GDL's, GDE's, fuel cells and processes of the invention are capable of being incorporated in the form of a variety of embodiments, only a few of which have been illustrated and described above.

Claims

1. A gas diffusion electrode comprising a gas diffusion layer with a surface to which platinum nanowires have been applied; wherein the surface is at least partially weakly hydrophobic or hydrophilic, forming a weakly hydrophobic and/or hydrophilic surface or weakly hydrophobic and/or hydrophilic regions on the surface.
2. A gas diffusion electrode according to claim 1 comprising a gas diffusion layer wherein when the surface is weakly hydrophobic or hydrophilic it has been treated by active screen plasma.
3. A gas diffusion electrode according to claim 1 or claim 2 comprising a gas diffusion layer which has a water contact angle less than 130°.
4. A gas diffusion electrode according to any preceding claim comprising a gas diffusion layer wherein the surface has a surface area in the range 50 - 100% weakly hydrophobic and/or hydrophilic.
5. A gas diffusion electrode according to any preceding claim wherein the platinum nanowires substantially cover the hydrophilic/weakly hydrophobic surface or hydrophilic/weakly hydrophobic regions on the surface.
6. A gas diffusion electrode according to any of claims 1 to 5 wherein the platinum nanowires cover in the range 75 - 99% of on the total surface.
7. A gas diffusion electrode according to any preceding claim wherein the platinum nanowires are uniformly distributed on the surface, the hydrophilic/weakly hydrophobic surface or hydrophilic/weakly hydrophobic regions on the surface.
8. A gas diffusion electrode according to any preceding claim wherein gas diffusion layer is selected from carbon cloth or carbon paper.

9. A gas diffusion electrode according to any preceding claim additionally comprising a gas diffusion layer having a porous layer.

10. A gas diffusion electrode according to any preceding claim wherein the platinum nanowires are of length in the range 50 - 500 nm, and/or of diameter in the range 1 - 10 nm.

11. A gas diffusion electrode according to any preceding claim wherein the platinum nanowires form a catalyst layer of thickness in the range 50 nm - 1 μ m.

12. A membrane electrode assembly comprising the gas diffusion electrode according to any preceding claim.

13. A fuel cell comprising the membrane electrode assembly according to claim 12 selected from direct methanol fuel cells and polymer electrode membrane fuel cells.

14. A process for making a gas diffusion electrode comprising the steps of:

- a. plasma treating a surface of a gas diffusion layer; and
- b. applying platinum nanowires to the plasma treated surface.

15. A process according to claim 12 wherein the platinum nanowires are applied to the plasma treated surface by being grown onto the plasma treated surface using a chemical reduction technique

16. A process according to claim 15 wherein the platinum nanowires form arrays.

17. A process according to claim 15 or claim 16 wherein the chemical reduction technique is the reduction of platinum containing precursors.

18. A process according to claim 17 wherein the platinum-containing precursor is selected from chloroplatinic acid (hexa)hydrate, platinic acid, sodium platinic chloride, potassium hexachloroplatinate, and combinations thereof.

19. A process according to claim 17 or claim 18 wherein reduction of the platinum-containing precursor uses a reducing agent selected from hydrogen, formic acid, ascorbic acid, citric acid, and combinations thereof.

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20. A process according to any of claims 17 to 19 wherein reduction of the platinum-containing precursor occurs in aqueous solution.

21. A process according to any of claims 17 to 20 wherein reduction of the platinum-containing precursor occurs at a temperature in the range 5 - 50°C.

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22. A gas diffusion layer, gas diffusion electrode, fuel cell or process substantially as described herein with reference to the examples and the drawings.

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Figure 1a

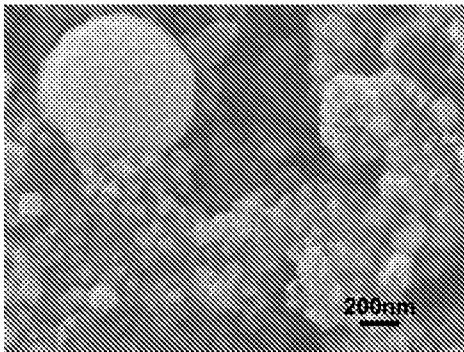
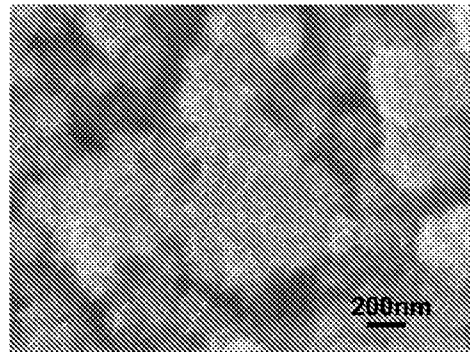


Figure 1b



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Figure 2a

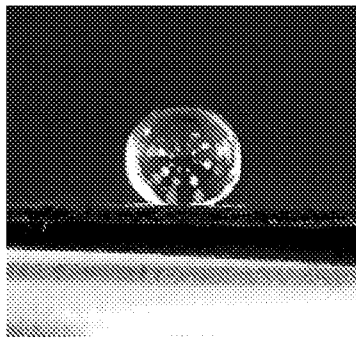
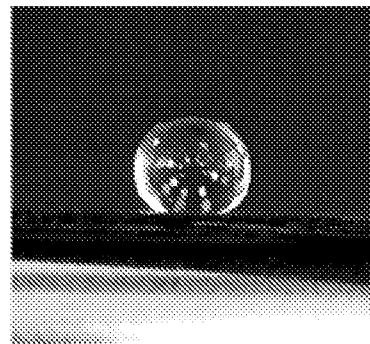


Figure 2b



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Figure 3

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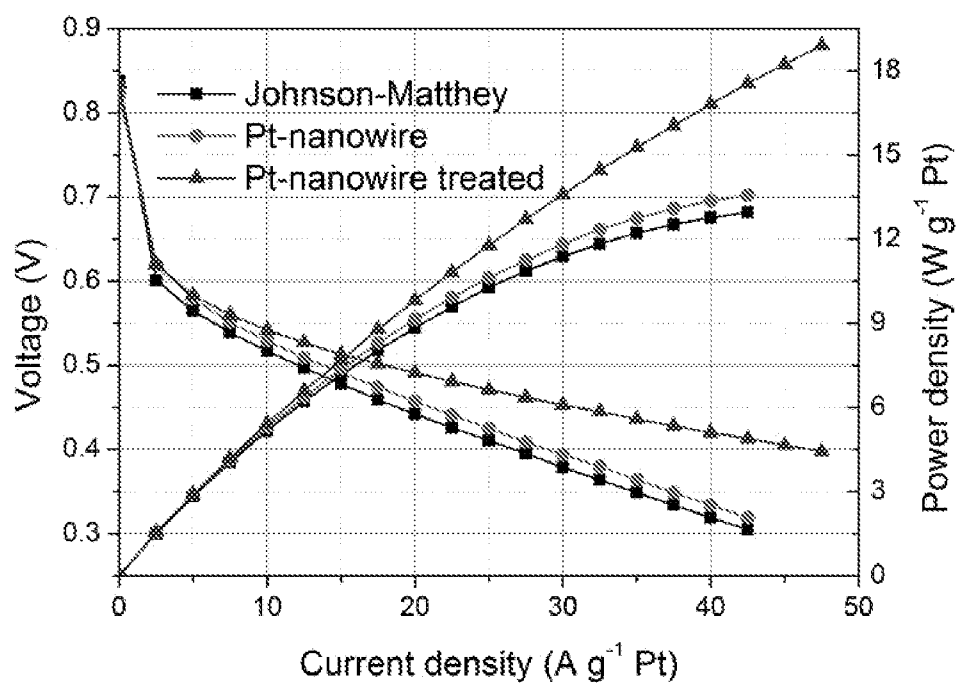
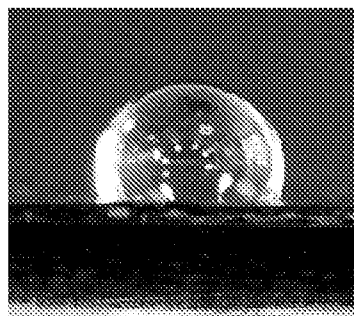
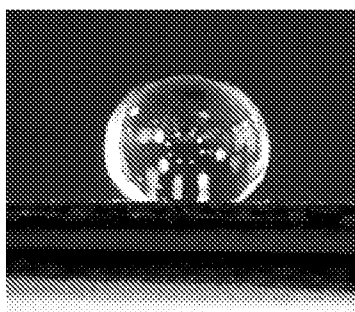


Figure 4a

Figure 4b

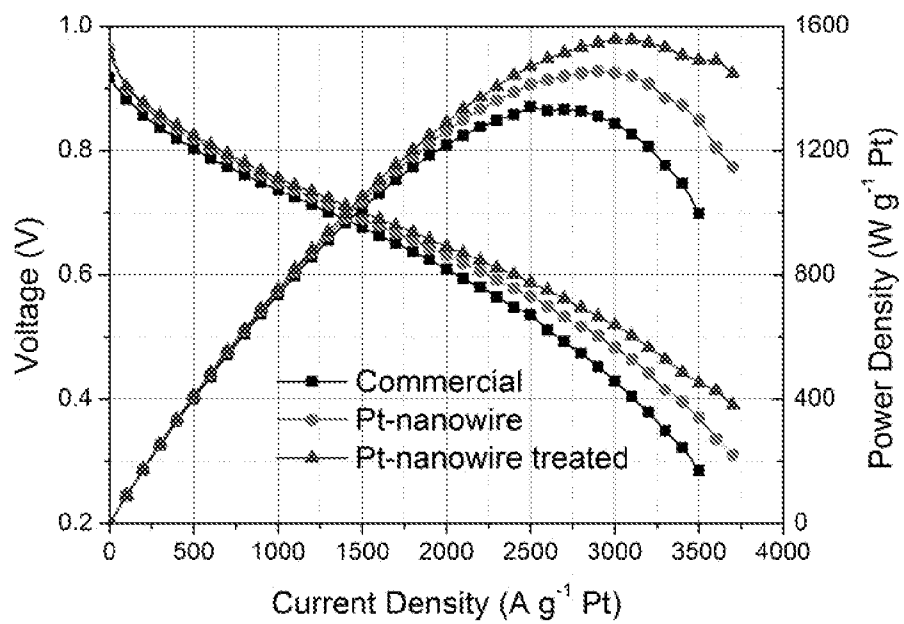
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Figure 5



INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2013/050393

A. CLASSIFICATION OF SUBJECT MATTER		
INV. H01M8/10	H01M4/86	H01M4/88 H01M4/92 H01M8/02
ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) H01M		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2008/305377 A1 (SHUI JIANGLAN [US] ET AL) 11 December 2008 (2008-12-11)	1-13,22
Y	page 4, paragraphs 61,66 - page 5, paragraph 76	14-21
Y	----- WO 2005/117176 A2 (UNIV MILANO BICOCCA [IT]; SEAL S P A; HYSYTEC S R L [IT]; RICCARDI CLA) 8 December 2005 (2005-12-08)	14-21
Y	page 6, lines 18-23 - page 8, lines 18-23 page 12, lines 28-29 ----- US 2005/064275 A1 (MEKALA DAVID R [US] ET AL) 24 March 2005 (2005-03-24)	14-21
	page 1, paragraph 12 - page 2, paragraphs 17,18; example 3 ----- -/-	
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 18 April 2013		Date of mailing of the international search report 29/04/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Boussard, Nadège

INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	DU ET AL: "A Facile Route for Polymer Electrolyte Membrane Fuel Cell Electrodes with in situ Grown Pt Nanowires", JOURNAL OF POWER SOURCES, ELSEVIER SA, CH, vol. 195, no. 1, 1 January 2010 (2010-01-01), pages 289-292, XP026564893, ISSN: 0378-7753, DOI: 10.1016/J.JPOWSOUR.2009.06.091 [retrieved on 2009-07-07] cited in the application page 290, paragraph 2.2 -----	1-22
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