(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
25 June 2015 (25.06.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/092371 A1

(51) International Patent Classification:
H01M 4/88 (2006.01) *C25B 11/04* (2006.01)
H01M 4/92 (2006.01) *H01M 8/10* (2006.01)

(21) International Application Number:
PCT/GB2014/053682

(22) International Filing Date:
12 December 2014 (12.12.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
1322494.4 19 December 2013 (19.12.2013) GB

(71) Applicant: **JOHNSON MATTHEY FUEL CELLS LIMITED** [GB/GB]; 5th Floor, 25 Farringdon Street, London EC4A 4AB (GB).

(72) Inventors: **BURTON, Sarah Louise**; 5 The Park, Lambourn, Nr Hungerford, Oxon RG17 8QQ (GB). **DICKINSON, Angus John**; 90 York Road, Swindon SN1 2JU (GB). **O'SULLIVAN, Julie**; 37 Darent Place, Didcot OX11 7UQ (GB).

(74) Agent: **SWIFT, Jane Elizabeth**; Johnson Matthey Process Technologies, PO Box 1, Belasis Avenue, Billingham, Cleveland TS23 1LB (GB).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

WO 2015/092371 A1

(54) Title: CATALYST LAYER

(57) Abstract: A catalyst layer comprising: (i) a platinum-containing electrocatalyst; (ii) oxygen evolution reaction electrocatalyst; (iii) one or more carbonaceous materials selected from the group consisting of graphite, nanofibres, nanotubes, nanographene platelets and low surface area, heat-treated carbon blacks wherein the one or more carbonaceous materials do not support the platinum-containing electrocatalyst; and (iv) proton-conducting polymer and its use in an electrochemical device is disclosed.

CATALYST LAYER

Field of the Invention

The present invention relates to a catalyst layer, which shows tolerance to high voltage situations, such as cell reversal and start-up shut-down incidences that occur in fuel cells. The invention also relates to electrodes, catalyst-coated membranes and membrane electrode assemblies comprising the catalyst layer.

Background of the Invention

A fuel cell is an electrochemical cell comprising two electrodes separated by an electrolyte. A fuel, e.g. hydrogen, an alcohol such as methanol or ethanol, or formic acid, is supplied to the anode and an oxidant, e.g. oxygen or air, is supplied to the cathode. Electrochemical reactions occur at the electrodes, and the chemical energy of the fuel and the oxidant is converted to electrical energy and heat. Electrocatalysts are used to promote the electrochemical oxidation of the fuel at the anode and the electrochemical reduction of oxygen at the cathode.

Fuel cells are usually classified according to the nature of the electrolyte employed. Often the electrolyte is a solid polymeric membrane, in which the membrane is electronically insulating but ionically conducting. In the proton exchange membrane fuel cell (PEMFC) the membrane is proton conducting, and protons, produced at the anode, are transported across the membrane to the cathode, where they combine with oxygen to form water.

A principal component of the PEMFC is the membrane electrode assembly (MEA), which is essentially composed of five layers. The central layer is the polymer ion-conducting membrane. On either side of the ion-conducting membrane there is an electrocatalyst layer, containing an electrocatalyst designed for the specific electrolytic reaction. Finally, adjacent to each electrocatalyst layer there is a gas diffusion layer. The gas diffusion layer must allow the reactants to reach the electrocatalyst layer and must conduct the electric current that is generated by the electrochemical reactions. Therefore the gas diffusion layer must be porous and electrically conducting.

Electrocatalysts for fuel oxidation and oxygen reduction are typically based on platinum or platinum alloyed with one or more other metals. The platinum or platinum alloy catalyst can be in the form of unsupported nanoparticles (such as metal blacks or other unsupported particulate metal powders) or can be deposited as even higher surface area particles onto a conductive carbon substrate or other conductive material (a supported catalyst).

Conventionally, the MEA can be constructed by a number of methods outlined hereinafter:

(i) The electrocatalyst layer may be applied to the gas diffusion layer to form a gas diffusion electrode. A gas diffusion electrode is placed on each side of an ion-conducting membrane and laminated together to form the five-layer MEA;

(ii) The electrocatalyst layer may be applied to both faces of the ion-conducting membrane to form a catalyst coated ion-conducting membrane. Subsequently, a gas diffusion layer is applied to each face of the catalyst coated ion-conducting membrane.

(iii) An MEA can be formed from an ion-conducting membrane coated on one side with an electrocatalyst layer, a gas diffusion layer adjacent to that electrocatalyst layer, and a gas diffusion electrode on the other side of the ion-conducting membrane.

Typically tens or hundreds of MEAs are required to provide enough power for most applications, so multiple MEAs are assembled to make up a fuel cell stack. Field flow plates are used to separate the MEAs. The plates perform several functions: supplying the reactants to the MEAs; removing products; providing electrical connections; and providing physical support.

High electrochemical potentials can occur in a number of real-life operational situations and in certain circumstances can cause damage to the catalyst layer/electrode structure, primarily due to corrosion of any carbon present in the layer, such as the support material for the catalyst. Such situations are well documented but include:

(i) Cell reversal: fuel cells occasionally are subjected to a voltage reversal (cell is forced to the opposite polarity). In addition to the loss of power associated with one or more cells going into voltage reversal, undesirable electrochemical reactions may occur which detrimentally affect fuel cell components.

(ii) Start-up shut-down: for many fuel cells it is not practical or economic to provide purging of hydrogen from the anode gas space with an inert gas such as nitrogen during shut down. This means there may arise a mixed composition of hydrogen and air on the anode whilst air is present on the cathode. Similarly, when a cell is re-started after being idle for some time, air may have displaced hydrogen from the anode and as hydrogen is re-introduced to the anode, again a mixed air/hydrogen composition will exist whilst air is present at the cathode. Under these circumstances an internal cell can exist, which leads to high potentials on the cathode.

Solutions proposed to address the problems associated with incidences of high electrochemical potentials include employing a catalyst that is more resistant to oxidative corrosion than conventional catalysts and incorporating an additional catalyst composition for

electrolysing water (water electrolysis thus occurs in preference to corrosion of any carbon support).

Summary of the Invention

For fuel cells to become commercially viable, particularly for automotive use, it is necessary to provide a high performance and stable catalyst layer, but with a low platinum loading. Using an unsupported "Pt black" catalyst in the catalyst layer compared to a carbon supported platinum catalyst can provide a more durable catalyst layer by avoiding the problems associated with carbon corrosion that occurs as a result of the high potentials caused by incidences of cell reversal and start-up shut-down. However, the present inventors have found that to produce a Pt black catalyst layer with the required structure for satisfactory operation and with sufficient uniformity and continuity of coating of the catalyst layer on the substrate, the platinum loading required is much higher than the requirements for commercialisation of many fuel cell applications, and in particular for automotive applications. The present inventors have surprisingly found that incorporation of a highly electrically conductive and corrosion resistant carbonaceous material into the catalyst layer enables suitable catalyst layer structures to be produced, that are also of excellent uniformity and continuity and that have a platinum loading in the catalyst layer consistent with automotive requirements.

The present invention provides a catalyst layer. The catalyst layer comprises: (i) a platinum-containing electrocatalyst; (ii) an oxygen evolution reaction electrocatalyst; (iii) one or more carbonaceous materials selected from the group consisting of graphite, nanofibres, nanotubes, nanographene platelets and low surface area, heat-treated carbon blacks, wherein the one or more carbonaceous materials do not support the platinum-containing electrocatalyst; and (iv) proton-conducting polymer.

The invention also provides an electrode, either an anode or cathode, comprising a gas diffusion layer and the catalyst layer of the invention.

The invention also provides a catalyst-coated membrane comprising a proton-conductive membrane and the catalyst layer of the invention.

Brief Description of the Drawings

Figure 1 shows the Beginning of Life (BOL) performance of Example 1 and Comparative Example 1.

Figure 2 shows the performance of Example 1 and Comparative Example 1 after incidences of cell reversal.

Detailed Description of the Invention

Preferred and/or optional features of the invention will now be set out. Any aspect of the invention may be combined with any other aspect of the invention, unless the context demands otherwise. Any of the preferred or optional features of any aspect may be combined, singly or in combination, with any aspect of the invention, unless the context demands otherwise.

Electrocatalyst

The electrocatalyst comprises platinum.

The platinum may be alloyed or mixed with one or more other platinum group metals (ruthenium, rhodium, palladium, osmium or iridium), gold, silver or a base metal or an oxide of one or more other platinum group metals, gold, silver or a base metal.

The platinum may be alloyed or mixed with one or more of ruthenium, nickel, cobalt, chromium, iridium, copper, iron, zinc, osmium, niobium, tantalum, vanadium, tin, titanium and rhodium.

The electrocatalyst is unsupported i.e. it is present as the 'black'.

Alternatively, the electrocatalyst is supported on a non-carbonaceous support (such as titania, niobia, tantala, tungsten carbide, hafnium oxide or tungsten oxide).

Alternatively, the electrocatalyst is supported on the oxygen evolution reaction catalyst.

In one embodiment, the platinum-containing electrocatalyst is unsupported, supported on a non-carbonaceous support or supported on the oxygen evolution reaction catalyst.

The electrocatalyst may be made by methods known to those in the art, for example by wet chemical methods.

In one embodiment, the electrocatalyst is a hydrogen oxidation reaction catalyst. The hydrogen oxidation reaction catalyst is platinum which may be alloyed with one or more other metals, such as osmium, ruthenium, niobium, tantalum, vanadium, iridium, tin, titanium or rhodium.

In a second embodiment, the electrocatalyst is an oxygen reduction reaction catalyst. The oxygen reduction reaction catalyst is platinum which may be alloyed with one or more other metals, such as nickel, cobalt, chromium, palladium, iridium, copper, iron or zinc.

Oxygen evolution reaction electrocatalyst

The oxygen evolution reaction (OER) catalyst is any catalyst known to those skilled in the art which catalyses the oxygen evolution reaction.

The oxygen evolution reaction catalyst suitably does not comprise platinum.

The oxygen evolution reaction catalyst may comprise ruthenium or ruthenium oxide or iridium or iridium oxide or mixtures thereof.

The oxygen evolution reaction catalyst may comprise iridium or iridium oxide and one or more metals M or an oxide thereof. M is a transition metal (other than iridium or ruthenium) or tin.

M may be a Group 4 metal: titanium, zirconium or hafnium.

M may be a Group 5 metal: vanadium, niobium or tantalum

M may be a Group 6 metal: chromium, molybdenum or tungsten.

M may be tin.

M may be selected from the group consisting of tantalum, titanium, zirconium, hafnium, niobium and tin; preferably tantalum, titanium and tin.

The iridium or oxide thereof and the one or more metals (M) or oxide thereof may either exist as mixed metals or oxides or as partly or wholly alloyed materials or as a combination thereof. The extent of any alloying can be shown by x-ray diffraction (XRD).

The atomic ratio of iridium to (total) metal M in the oxygen evolution catalyst is from 20:80 to 99:1, suitably 30:70 to 99:1 and preferably 60:40 to 99:1.

Such oxygen evolution catalysts may be made by methods known to those in the art, for example by wet chemical methods.

The oxygen evolution reaction catalyst may comprise a mixed metal oxide of formula

$$(AA')_a(BB')_bO_c.$$

wherein A and A' are the same or different and are selected from the group consisting of yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, magnesium, calcium, strontium, barium, sodium, potassium, indium, thallium, tin, lead, antimony and bismuth; B is selected from the group consisting of Ru, Ir, Os, and Rh; B' is selected from the group consisting of Ru, Ir, Os, Rh, Ca, Mg or RE (wherein RE is a rare earth metal); c is from 3-11; the atomic ratio of (a+b):c is from 1:1 to 1:2; the atomic ratio of a:b is from 1: 1.5 to 1.5:1.

A and A' may be selected from the group consisting of: sodium, potassium, calcium, strontium, barium, lead and cerium.

B may selected from the group consisting of Ru, Ir, Os, Rh (suitably Ru and Ir) having an oxidation state of from 3^+ to 6^+, including intermediate partial oxidation states.

B' may be selected from the group consisting of Ru, Ir, Os, Rh (suitably Ru and Ir) having an oxidation state of from 3^+ to 6^+, including intermediate partial oxidation states, Ca,

Mg, RE (wherein RE is as hereinafter defined), indium, thallium, tin, lead, antimony and bismuth.

c is from 3-11. Since the atomic ratio of (a+b):c is known, the value of (a+b) can be determined. Similarly, since the atomic ratio of a:b and the value of (a+b) is known, the values of a and b can be determined.

Specific examples of crystalline metal oxides which may be used as the oxygen evolution catalyst include, but are not limited to: $RERuO_3$; $SrRuO_3$; $PbRuO_3$; $REIrO_3$; $CaIrO_3$; $BaIrO_3$; $PbIrO_3$; $SrIrO_3$; $KIrO_3$; $SrM_{0.5}Ir_{0.5}O_3$; $Ba_3LiIr_2O_9$; Sm_2NaIrO_6; $La_{1.2}Sr_{2.7}IrO_{7.33}$; $Sr_3Ir_2O_7$; $Sr_2Ir_3O_9$; $SrIr_2O_6$; $Ba_2Ir_3O_9$; $BaIr_2O_6$; $La_3Ir_3O_{11}$; $RE_2Ru_2O_7$; $RE_2Ir_2O_7$; $Bi_2Ir_2O_7$; $Pb_2Ir_2O_7$; $Ca_2Ir_2O_7$; $(NaCa)_2Ir_2O_6$; $(NaSr)_3Ir_3O_{11}$; $(NaCe)_2Ir_2O_7$; $(NaCe)_2Ru_2O_7$; $(NaCe)_2(RuIr)_2O_7$.

In the above specific examples: RE is one or more rare earth metals selected from the group consisting of: yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium; M is Ca, Mg or RE (where RE is as defined before).

These crystalline mixed metal oxides may be prepared by methods known in the art, such as described in WO2012/080726.

The oxygen evolution catalyst may be unsupported.

Alternatively, the oxygen evolution catalyst may be supported on at least some of the one or more carbonaceous materials selected from the group consisting of graphite, nanofibres, nanotubes, nanographene platelets and low surface area, heat-treated carbon blacks, or on a non-carbonaceous support (such as titania, niobia, tantala, tungsten carbide, hafnium oxide or tungsten oxide).

Carbonaceous material

The electrically conductive material may be graphite. Graphite is a crystalline allotropic form of carbon which has a layered, planar structure; in each layer, the carbon atoms are arranged in a hexagonal crystalline lattice. Graphite exists either in natural or synthetic form and is suitably used in its synthetic form.

The graphite may be particulate graphite, e.g. flake graphite, spherical graphite or graphite powder. The particle size of as-received graphite materials can vary over a wide range for different grades, typically from as low as 3 micron to as high as 500 micron diameter. The preferred graphite materials have a D50 (i.e. 50% of the particles are below a specific particle size) particle size range of from 3-4 micron up to around 20 micron, but are able to be broken down into smaller particles during processing to form the catalyst layer structures.

The graphite has a low specific surface area (as measured using the well-known BET method), for example a specific surface area less than $40m^2/g$, for example less than 20 m^2/g.

Examples of such graphite materials include products available from Timcal Graphite & Carbon under the tradenames TIMREX™ and C-NERGY™, from Branwell Graphite Ltd such as V-SGA5 and from Alfa Aesar, such as product 46304.

The carbonaceous material may be fibrous or tubular nanofibres or nanotubes, such as Pyrograf III® Carbon Fiber from Pyrograf Products Inc. or VGCF-H from Showa Denko K.K..

The carbonaceous material may be nanographene platelets, such as N008 or N006 from Angston Materials LLC.

The carbonaceous material may be a low surface area, heat-treated carbon black, for example graphitised Vulcan XC72R, which is available from Cabot Corporation. Low surface area, heat treated carbon blacks have an amorphous structure and are obtained by heat treating a commercially available carbon black in an inert atmosphere at a temperature of greater than 1500°C, suitably greater than 2000°C.

The carbonaceous materials used in the present invention have a surface area (as measured using the well-known BET method) of less than $100m^2/g$, suitably less than $80m^2/g$, suitably less than $40m^2/g$ and preferably less than $20m^2/g$.

Suitably, the one or more carbonaceous materials is selected from the group consisting of graphite, nanofibres, nanotubes and nanographene platelets; preferably, the one or more carbonaceous materials includes graphite, and most preferably, the carbonaceous material is graphite.

The one or more carbonaceous materials do not support the platinum-containing electrocatalyst. Suitably, the one or more carbonaceous materials do not support the oxygen evolution catalyst.

Proton-conducting polymer

The proton-conducting polymer is any polymer that is capable of conducting protons. Examples of such polymers include dispersions of polymers based on perfluorosulphonic acid (PFSA) polymers (such as those sold under the trade names Nafion® (E.I. DuPont de Nemours and Co.), Aquivion® (Solvay Speciality Polymers), Aciplex® (Asahi Kasei) and Flemion® (Asahi Glass KK). Such PFSA based ion-conducting polymers are formed from the copolymerisation of tetrafluoroethylene and a perfluorinated sulphonic acid derivative.

As an alternative to PFSA ion-conducting polymers it is possible to use dispersions of ion-conducting polymers based on sulfonated or phosphonated hydrocarbon polymers, such as the polyaromatic class of polymers.

Catalyst layer

The catalyst layer may comprise additional components. Such components include, but are not limited to: a hydrophobic (a polymer such as PTFE or an inorganic solid with or without surface treatment) or a hydrophilic (a polymer or an inorganic solid, such as an oxide) additive to control water transport; an additional catalytic material for example having activity for the decomposition of hydrogen peroxide (e.g. ceria or manganese dioxide) or for improving the carbon monoxide tolerance of the catalyst layer (e.g. tantalum, niobium, rhodium). Any additional catalytic material may be supported or unsupported; if supported, it may be supported on at least some of the one or more carbonaceous materials selected from the group consisting of graphite, nanofibres, nanotubes, nanographene platelets and low surface area, heat-treated carbon blacks, or on a non-carbonaceous support (such as titania, niobia, tantala, tungsten carbide, hafnium oxide or tungsten oxide).

To prepare the catalyst layer the platinum-containing electrocatalyst, oxygen evolution reaction electrocatalyst, one or more carbonaceous materials and proton-conducting polymer, and any additional components, are dispersed in an aqueous and/or organic solvent, to prepare a catalyst ink. If required, particle break-up is carried out by methods know in the art, such as high shear mixing, milling, ball milling, passing through a microfluidiser etc or a combination thereof, to achieve uniformity of particle size.

After preparation of the catalyst ink, the ink is deposited onto a substrate (e.g. gas diffusion layer, proton exchange membrane or transfer substrate) to form the catalyst layer. The ink may be deposited by standard methods such as printing, spraying, knife over roll, powder coating, electrophoresis etc.

The catalyst layer is suitably ≥ 1 μm; more suitably ≥ 2 μm in thickness.

The catalyst layer is suitably ≤ 20μm; more suitably ≤ 15 μm in thickness; preferably ≤ 10 μm in thickness.

The loading of platinum (from the platinum-containing electrocatalyst) in the catalyst layer is ≤ 0.8 mg/cm^2, suitably ≤ 0.4 mg/cm^2.

The loading of platinum (from the platinum-containing electrocatalyst) in the catalyst layer is ≥ 0.01 mg/cm^2, suitably ≥ 0.025 mg/cm^2.

The exact loading of platinum (from the platinum-containing electrocatalyst) in the catalyst layer is dependent upon whether the catalyst layer is for use at the anode or the cathode and determination of appropriate loadings will be known to those skilled in the art. For example, for use at the anode a platinum loading of 0.02 – 0.15mg/cm^2 is appropriate. For use at the cathode, a higher platinum loading of 0.1 – 0.8mg/cm^2 is appropriate

Suitably, the ratio (by weight) of the oxygen evolution catalyst to total platinum-containing electrocatalyst (platinum + any alloying metal) in the catalyst layer is from 20:1 to 1:20, preferably from 1:1 to 1:10. The actual ratio will depend on whether the catalyst layer is employed at the anode or cathode and whether the oxygen evolution catalyst is used as a support for the electrocatalyst.

The ratio (by weight) of the platinum in the platinum-containing electrocatalyst to the one or more carbonaceous materials is from 5:95 to 95:5, suitably 10:90 to 90:10 and more suitably 40:60 to 90:10.

The catalyst layer of the invention has utility in an electrochemical device, and has particular utility in a membrane electrode assembly for a PEMFC.

The invention provides a gas diffusion electrode comprising a gas diffusion layer and a catalyst layer of the invention.

To prepare a gas diffusion electrode the catalyst ink is deposited directly onto a gas diffusion layer (GDL) for example by one of the methods previously described. Alternatively, the catalyst layer is first formed on a transfer substrate (such as a polymeric material such as polytetrafluoroethylene (PTFE) polyimide, polyvinylidene difluoride (PVDF), or polypropylene (for example biaxially-oriented polypropylene, BOPP) by deposition of a catalyst ink as hereinbefore described onto the transfer substrate. The catalyst layer may then be transferred to the GDL using a decal transfer technique known to those skilled in the art.

The GDLs are suitably based on conventional non-woven carbon fibre gas diffusion substrates such as rigid sheet carbon fibre papers (e.g. the TGP-H series of carbon fibre papers available from Toray Industries Inc., Japan) or roll-good carbon fibre papers (e.g. the H2315 based series available from Freudenberg FCCT KG, Germany; the Sigracet® series available from SGL Technologies GmbH, Germany; the AvCarb® series available from Ballard Material Products, United States of America; or the N0S series available from CeTech Co., Ltd. Taiwan), or on woven carbon fibre cloth substrates (e.g. the SCCG series of carbon cloths available from the SAATI Group, S.p.A., Italy; or the W0S series available from CeTech Co., Ltd, Taiwan). For many PEMFC applications the non-woven carbon fibre paper, or woven carbon fibre cloth substrates are typically modified with a hydrophobic polymer treatment and/or application of a

microporous layer comprising particulate material either embedded within the substrate or coated onto the planar faces, or a combination of both, to form the gas diffusion layer. The particulate material is typically a mixture of carbon black and a polymer such as polytetrafluoroethylene (PTFE). Suitably the gas diffusion layers are between 100 and 300μm thick. Preferably there is a layer of particulate material such as carbon black combined with PTFE on the faces of the gas diffusion layers that contact the electrocatalyst layers.

The invention also provides a catalyst coated membrane (CCM) comprising a proton exchange membrane (having a first and second face) and a catalyst layer of the invention. The catalyst layer of the invention may be on the first face or the first and second faces of the proton exchange membrane. The catalyst layer components are formulated into an ink as hereinbefore described and the ink deposited onto the first or first and second faces of the proton exchange membrane using techniques such as spraying, printing and doctor blade methods. Alternatively, the catalyst layer is first formed on a transfer substrate (as hereinbefore described) and transferred onto the proton exchange membrane using a decal transfer technique known to those skilled in the art.

The proton exchange membrane may be any membrane suitable for use in a PEMFC, for example the membrane may be based on a perfluorinated sulphonic acid material such as Nafion® (DuPont), Aquivion® (Solvay Specialty Polymers), Flemion® (Asahi Glass KK) and Aciplex® (Asahi Kasei). Alternatively, the membrane may be based on a sulphonated hydrocarbon membrane such as those available from FuMA-Tech GmbH as the fumapem® P, E or K series of products, JSR Corporation, Toyobo Corporation, and others. Alternatively, the membrane may be based on polybenzimidazole doped with phosphoric acid which will operate in the range 120°C to 180°C. Other components may be added to the membrane, for example to improve the durability, as will be known to those in the art.

The proton exchange membrane may be a composite membrane, wherein the membrane contains other materials that confer properties such as mechanical strength. For example, the membrane may contain a porous reinforcing material, such as an expanded PTFE material.

The proton exchange membrane may also comprise one or more components which assist the chemical durability of the membrane, for example a hydrogen peroxide decomposition catalyst, a radical scavenger etc.

The invention also provides a MEA comprising a catalyst layer, a gas diffusion electrode or a catalyst coated membrane of the invention and an electrochemical device, such as a fuel cell, comprising a MEA, catalyst layer, gas diffusion electrode or catalyst coated membrane of the invention.

Although the invention is described with reference to its use in a PEMFC, it can be understood that the catalyst layer of the invention will have application in other types of fuel cells where the high voltage situations as described can occur. In addition the catalyst layer of the invention may find application in other electrochemical devices, such as at the oxygen evolution/reduction electrode of a regenerative fuel cell or the oxygen evolution electrode of an electrolyser.

Examples

The invention will be described further with reference to the following examples, which is illustrative and not limiting of the invention.

Example 1

An anode catalyst ink was prepared by mixing an unsupported platinum black catalyst (Johnson Matthey, HiSPEC 1000) with an aqueous dispersion of a perfluorosulphonic acid ionomer of equivalent weight 790 (Solvay Plastics, D79-25BS Dispersion) at a level of 16wt% ionomer relative to the weight of platinum. The aqueous solution had a total solids content of 45%. The platinum black powder was added to the diluted ionomer dispersion at 65°C with stirring. This dispersion was mixed using a high shear mixer to ensure the components were evenly dispersed before processing through a bead mill, to reduce the particle size of the Pt catalyst. An oxygen evolution catalyst (Johnson Matthey, IrO_2/TaO_2 prepared as described in WO2011/021034) was added to the diluted ink to achieve a ratio by weight of 1.0:1.26 Pt:IrO_2/TaO_2. The catalyst was gently stirred into the ink to ensure even distribution. After processing the ink was diluted with neat propan-1-ol to 35% total solids (propanol concentration 30.9% total ink).

Synthetic graphite powder (Alfa Aesar, 46304), with an as-received average particle size of 7-11 micron, was dispersed in neat propan-1-ol. The graphite dispersion was mixed using a high shear mixer and added to the Pt black/ionomer dispersion to give a weight ratio Pt to graphite of 1:0.36. The amount of propan-1-ol added to the graphite was calculated to give a final ink solids content of 16%. The final ink was passed through a high pressure homogeniser several times to further break down the particles and to ensure a homogeneous composition. Characterisation of the ink via particle size analysis, measured in a 22% propan-1-ol/water solution revealed that the D50 of the particles (i.e. combined catalyst, graphite and ionomer particles) was 2.5 micron.

The anode catalyst layer was prepared by depositing the anode catalyst ink onto a PTFE decal-transfer substrate and drying to achieve a continuous anode catalyst layer with a Pt metal loading of 0.08 $mgPtcm^{-2}$ as measured by XRF, and thickness of 2-3μm. The same process was used to produce a cathode catalyst layer decal at 0.4 $mgPtcm^{-2}$ from a cathode ink containing a supported 50%Pt/carbon catalyst and 80% ionomer with respect to the weight of the carbon. The anode and cathode catalyst layer decals were positioned either side of a perfluorosulphonic acid membrane and hot pressed to produce a CCM. Appropriate seals and GDLs were added to allow compatibility with the fuel cell single cell hardware and the resultant MEAs were evaluated for beginning of life (BOL) performance and cell reversal tolerance.

Comparative Example 1

A comparative MEA was prepared using the same methodology as described for Example 1. The anode electrocatalyst was a conventional carbon black supported platinum catalyst (Johnson Matthey, 60wt%Pt/Ketjen EC300J carbon) and the ionomer dispersion was added to a level of 80wt% ionomer relative to the weight of the carbon support. The anode layer formulation comprised the same ionomer type as Example 1, the same Pt loading, and the same OER catalyst, but does not comprise any graphite. The ratio of Pt to OER catalyst was 1.0:0.86 $Pt:IrO_2/TaO_2$. The other components of Comparative Example 1 i.e. the GDL, seals, PFSA membrane and the cathode catalyst layer were identical to those used in Example 1.

A summary of the Example 1 and Comparative Example 1 is given in Table 1.

Table 1

	Example 1	**Comparative Example 1**
Electrocatalyst	Pt Black	60wt% Pt/ketjen EC300J
Oxygen evolution reaction catalyst	IrO_2/TaO_2	IrO_2/TaO_2
Carbonaceous material	Graphite	N/A
Proton-conducting polymer	PFSA EW 790	PFSA EW 790
Platinum loading	0.08 $mgPt/cm^2$	0.08 $mgPt/cm^2$
Catalyst layer thickness	2-3 μm	2-3 μm
Pt-containing electrocatalyst : OER catalyst	1.0 : 1.26	1.0 : 0.86
Pt : carbonaceous material	1: 0.36	N/A

Example 1 and the Comparative Example 1 were both tested in the same single cell hardware under the same test conditions. Following positioning between the bi-polar plates of the cell, the MEA was placed under compression, the cell was heated and reactant gases and humidification supplied. The MEAs were conditioned and a beginning of life MEA performance polarisation plot (voltage vs. current) was measured under a range of operating conditions, including a test with H_2/Air, at 1.5/2.0 stoichiometry, 65°C, 50% relative humidity and ambient pressure. The results for Example 1 and the Comparative Example 1 (Comparative MEA) are shown in Figure 1. The MEAs show a very similar voltage and resistance response across the current density range demonstrating that the same BOL performance can be attained from the anode catalyst layer of the invention in comparison to the more conventional carbon supported Pt/carbon catalyst based anode layer.

Following the BOL performance test the MEA performance stability during a highly accelerated anode reversal test was evaluated. The MEA was conditioned at 65°C, 50%RH and ambient pressure while supplied with H_2 and synthetic air ($21\%O_2/79\%N_2$) at 1.5/2.0 stoichiometry. The anode gas was then changed from H_2 to N_2. A load of $200mAcm^{-2}$ was then drawn from the cell to simulate a reversal event caused by gas starvation to the anode side. The cell voltage, resistance and CO_2 content of anode exhaust was monitored for the 5 minute duration of the reversal event, after which time H_2 was re-supplied to the anode, and air to the cathode. The cell was reconditioned and a performance and resistance measurement performed under the same conditions as at BOL to determine the impact of the reversal event. The procedure was repeated until a 50 mV loss at 1.2 Acm^{-2} on H_2/air was observed. This point was denoted as the end-of-life (EOL) criteria. An anode diagnostic test was also performed at BOL and after each reversal event in which the performance was measured using a H_2/N_2 (75:25) anode gas composition to evaluate any changes to anode mass transport losses throughout the test. Figure 2 compares the performance at 1.2 Acm^{-2} after multiple reversal events for Example 1 and Comparative Example 1 (Comparative MEA) over the duration of the test. Superior retention of MEA performance is clearly observed for Example 1 vs. the Comparative Example 1 under both H_2/air and in the H_2/N_2 /air diagnostic test. Comparative Example 1 reached the EOL criteria after only 21 reversal cycles, whilst Example 1 was clearly superior and was able to withstand 102 reversal cycles before reaching the EOL point. This benefit is ascribed to the improved layer formulation of Example 1 minimising anode layer degradation via carbon corrosion (CO_2). This effect is seen in both the H_2/N_2 anode diagnostic test in Figure 2 and the measured CO_2 in the anode exhaust during the reversal events. For Example 1 the CO_2 content

of the anode exhaust was always measured to below 100 ppm, whilst for the Comparative MEA CO_2 levels up to 470 ppm were measured in the anode exhaust.

CLAIMS

1. A catalyst layer comprising: (i) a platinum-containing electrocatalyst; (ii) oxygen evolution reaction electrocatalyst; (iii) one or more carbonaceous materials selected from the group consisting of graphite, nanofibres, nanotubes, nanographene platelets and low surface area, heat-treated carbon blacks wherein the one or more carbonaceous materials do not support the platinum-containing electrocatalyst; and (iv) proton-conducting polymer.

2. A catalyst layer according to claim 1, wherein the platinum-containing electrocatalyst is unsupported, supported on a non-carbonaceous support or supported on the oxygen evolution catalyst.

3. A catalyst layer according to claim 1 or 2, wherein the platinum-containing electrocatalyst is unsupported.

4. A catalyst layer according to any preceding claim, wherein the one or more carbonaceous materials have a surface area of less than $100m^2/g$.

5. A catalyst layer according to any preceding claim, wherein the one or more carbonaceous materials includes graphite.

6. A catalyst layer according to any preceding claim, wherein the one or more carbonaceous materials do not support the oxygen evolution catalyst.

7. A catalyst layer according to any preceding claim, wherein the catalyst layer is $\geq 1\mu m$ in thickness.

8. A catalyst layer according to any preceding claim, wherein the catalyst layer is $\leq 20\mu m$ in thickness.

9. A catalyst layer according to any preceding claim, wherein the loading of platinum is $\leq 0.8mg/cm^2$.

10. A catalyst layer according to any preceding claim, wherein the loading of platinum is $\geq 0.01 mg/cm^2$.

11. A catalyst layer according to any preceding claim, wherein the ratio by weight of the platinum in the platinum-containing electrocatalyst to carbonaceous material is from 5:95 to 95:5.

12. The use of a catalyst layer according to any preceding claim in an electrochemical device.

13. An electrode comprising a gas diffusion layer and a catalyst layer according to any one of claims 1 to 11.

14. An electrode according to claim 13, wherein the electrode is an anode.

15. A catalyst-coated membrane comprising a proton-conductive membrane and a catalyst layer according to any one of claims 1 to 11.

16. A membrane electrode assembly comprising a catalyst layer according to any one of claims 1 to 11, an electrode according to any one of claims 13 and 14, or a catalyst-coated membrane according to claim 15.

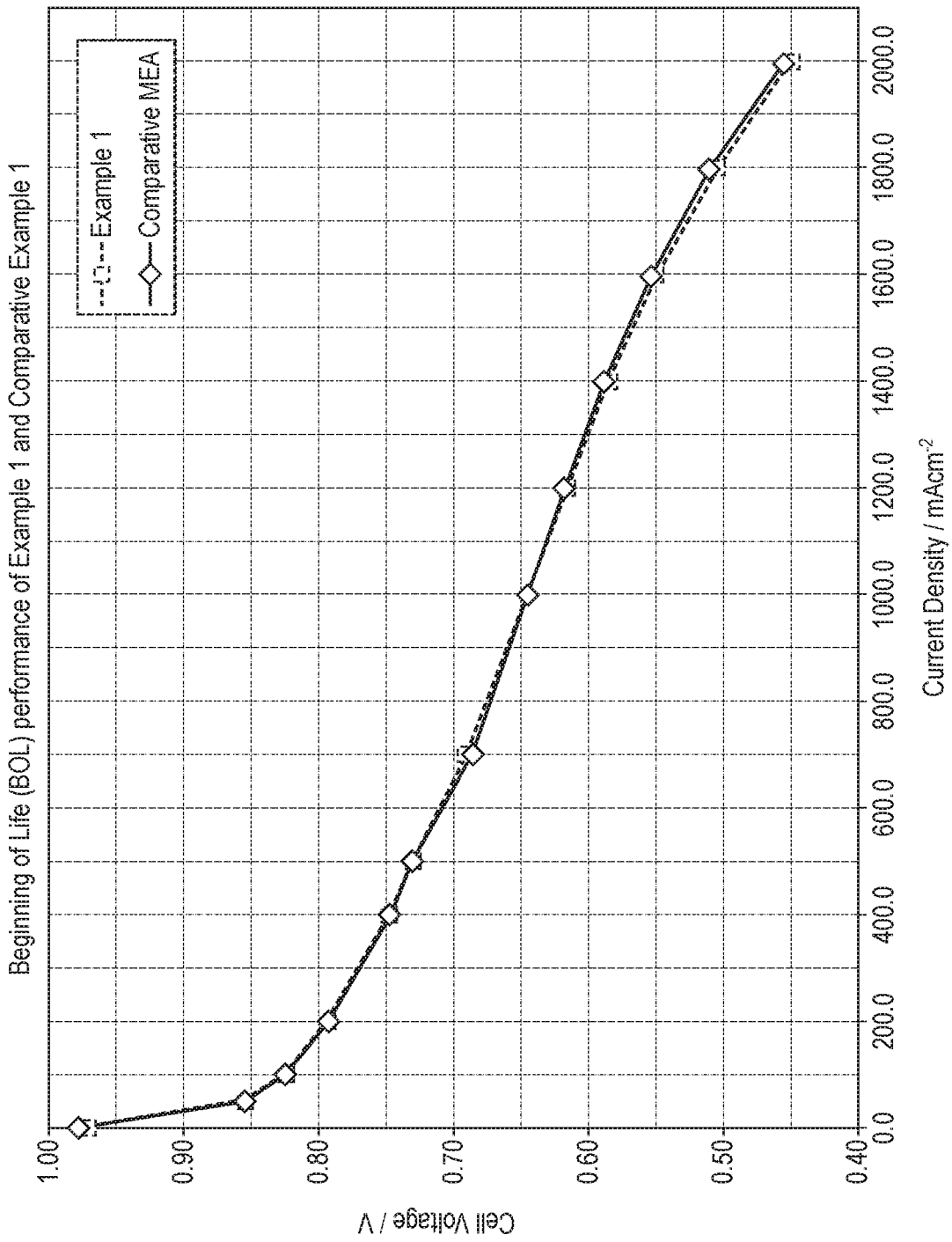

Beginning of Life (BOL) performance of Example 1 and Comparative Example 1
Example 1
Comparative MEA
Cell Voltage / V
1.00
0.90
0.80
0.70
0.60
0.50
0.40
Current Density / mAcm-2
0.0
200.0
400.0
600.0
800.0
1000.0
1200.0
1400.0
1600.0
1800.0
2000.0

FIG. 1

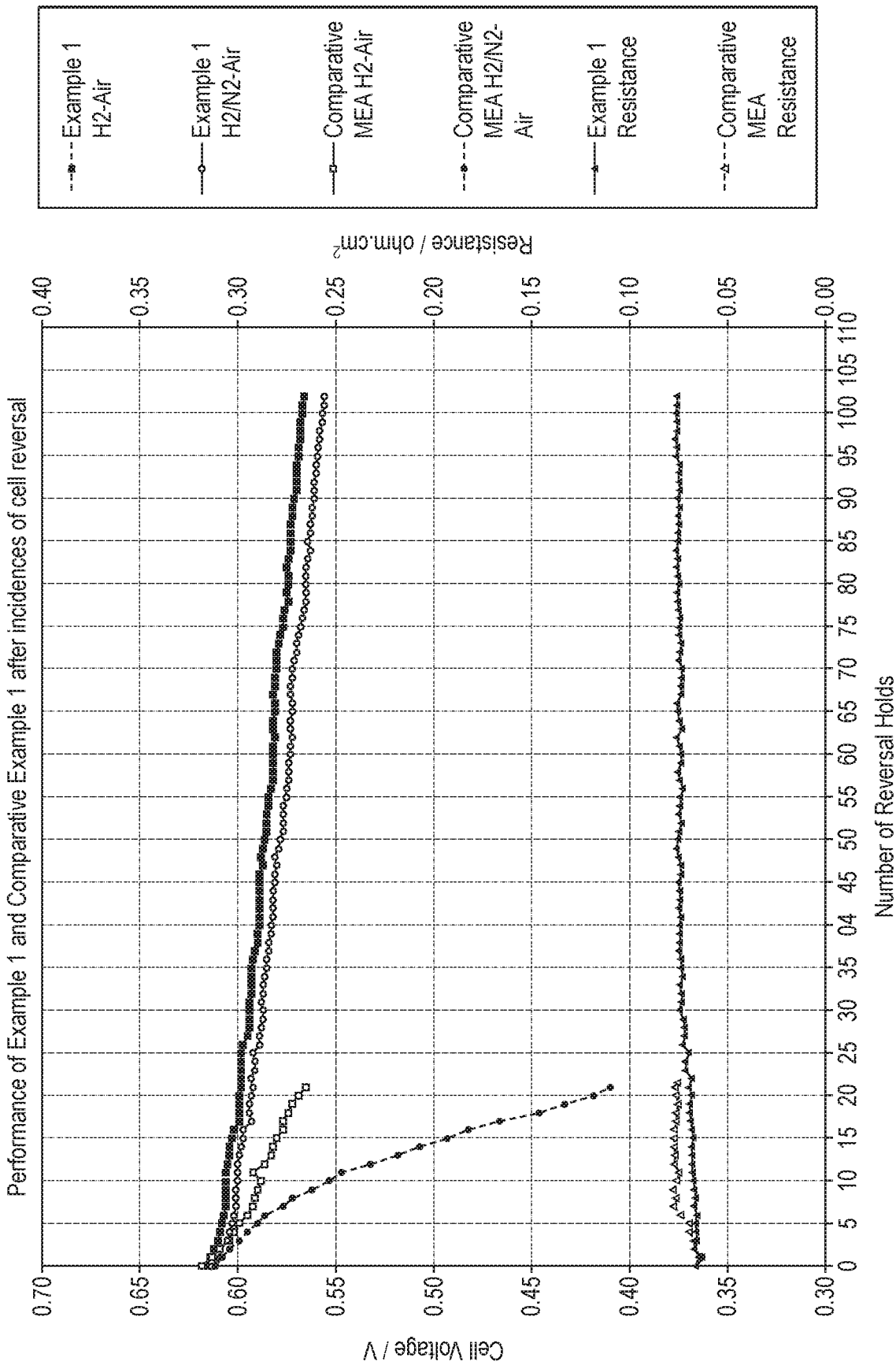

Example 1 H2-Air
Example 1 H2/N2-Air
Comparative MEA H2-Air
Comparative MEA H2/N2-Air
Example 1 Resistance
Comparative MEA Resistance
Performance of Example 1 and Comparative Example 1 after incidences of cell reversal
Cell Voltage / V
Resistance / ohm.cm²
Number of Reversal Holds
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0 5 10 15 20 25 30 35 04 45 50 55 60 65 70 75 80 85 90 95 100 105 110

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2014/053682

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M4/88 H01M4/92 C25B11/04 H01M8/10
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 C25B

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	WO 2011/021034 A1 (JOHNSON MATTHEY PLC [GB]; SHARMAN JONATHAN DAVID BRERETON [GB]; THEOBA) 24 February 2011 (2011-02-24) page 1, line 1 - page 2, line 2; claims 1-13 page 5, line 20 - page 7, line 2 page 7, line 8 - line 30 page 8, line 13 - line 20 line 9 - page 9, line 25 page 9, line 28 - page 10, line 2 table 1 examples 1,3,4 claims 1-14 figure 3	1-16

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[X] Further documents are listed in the continuation of Box C.

[X] 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

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 January 2015	11/02/2015

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Kuhn, Tanja

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2014/053682

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP S62 17193 A (SHIRAKAWA SEISAKUSHO KK; MOTOO SATORU; FURUYA CHOICHI) 26 January 1987 (1987-01-26) abstract	1
A	GB 2 009 792 A (GEN ELECTRIC) 20 June 1979 (1979-06-20) the whole document	1-16
A	EP 2 475 034 A1 (SOLVICORE GMBH & CO KG [DE]) 11 July 2012 (2012-07-11) paragraph [0001] paragraph [0003] - paragraph [0004]	1-16
A	& US 2009/068541 A1 (YAN SUSAN G [US] ET AL) 12 March 2009 (2009-03-12) claims 1-26	1-16
A	WO 2006/062947 A2 (NANOSYS INC [US]; NIU CHUNMING [US]; BOCK LAWRENCE A [US]; CHOW CALVIN) 15 June 2006 (2006-06-15) paragraph [0020] - paragraph [0021] claims 1,2,11,13,17,18,19, 28	1-16
A	WO 2006/124959 A2 (BROOKHAVEN SCIENCE ASS LLC [US]; ADZIC RADOSLAV R [US]; ZHANG JUNLIANG) 23 November 2006 (2006-11-23) paragraph [0003] - paragraph [0006] paragraph [0009] paragraph [0012] paragraph [0014] paragraph [0021] paragraph [0087] - paragraph [0088] paragraph [0094] paragraph [0099] claims 2,22, 37,43-47	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2014/053682

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2011021034 A1	24-02-2011	CN 102484259 A	30-05-2012
		EP 2467890 A1	27-06-2012
		JP 2013502682 A	24-01-2013
		KR 20120056848 A	04-06-2012
		US 2012214084 A1	23-08-2012
		WO 2011021034 A1	24-02-2011
JP S6217193 A	26-01-1987	JP H0124868 B2	15-05-1989
		JP S6217193 A	26-01-1987
GB 2009792 A	20-06-1979	CA 1125697 A1	15-06-1982
		DD 143932 A5	17-09-1980
		DE 2844499 A1	13-06-1979
		ES 475786 A1	16-01-1980
		ES 481257 A1	16-02-1980
		FR 2411248 A1	06-07-1979
		GB 2009792 A	20-06-1979
		IN 150899 A1	08-01-1983
		IT 1104585 B	21-10-1985
		JP S5495996 A	28-07-1979
		JP S6127472 B2	25-06-1986
		MX 148462 A	25-04-1983
		NL 7811996 A	12-06-1979
		PL 211561 A1	25-02-1980
		SE 7812641 A	10-06-1979
		US 4210501 A	01-07-1980
EP 2475034 A1	11-07-2012	CA 2822106 A1	28-06-2012
		CN 103270631 A	28-08-2013
		EP 2475034 A1	11-07-2012
		JP 2014505330 A	27-02-2014
		KR 20140012049 A	29-01-2014
		US 2013330652 A1	12-12-2013
		WO 2012085245 A1	28-06-2012
WO 2006062947 A2	15-06-2006	AU 2005314211 A1	15-06-2006
		CA 2588548 A1	15-06-2006
		CN 101107737 A	16-01-2008
		CN 101707256 A	12-05-2010
		CN 102593466 A	18-07-2012
		EP 1829141 A2	05-09-2007
		EP 2432058 A1	21-03-2012
		JP 5277451 B2	28-08-2013
		JP 2008523565 A	03-07-2008
		KR 20070086981 A	27-08-2007
		US 2006188774 A1	24-08-2006
		US 2009017363 A1	15-01-2009
		US 2010233585 A1	16-09-2010
		US 2011229795 A1	22-09-2011
		US 2012282540 A1	08-11-2012
		WO 2006062947 A2	15-06-2006
WO 2006124959 A2	23-11-2006	CA 2607871 A1	23-11-2006
		CN 101180123 A	14-05-2008
		EP 1883468 A2	06-02-2008
		HK 1119619 A1	19-04-2013
		JP 5518330 B2	11-06-2014
		JP 2008545604 A	18-12-2008

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2014/053682

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		KR 20080007622 A	22-01-2008
		US 2006263675 A1	23-11-2006
		US 2007264189 A1	15-11-2007
		US 2011151356 A1	23-06-2011
		WO 2006124959 A2	23-11-2006