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(54) Title: CATALYST MATERIAL WITH IMPROVED SPECIFIC ACTIVITY

(57) Abstract: The present invention relates to a catalyst material with an improved specific activity for electrochemical reduction reactions. In particular the present invention relates to a catalyst material for use in catalysing the oxygen reduction reaction at the cathode in a fuel cell.

Catalyst material with improved specific activity

Field of invention

The present invention relates to a catalyst material with an improved specific activity for electrochemical reduction reactions. In particular the present invention relates to a catalyst material for use in catalysing the oxygen reduction reaction at the cathode in a fuel cell.

Background of invention

Fuel cells are electrochemical devices that directly convert chemical energy to electrical energy. Fuel cells consist of an electrolyte medium, which is sandwiched between two electrodes. One electrode, the anode, facilitates electrochemical oxidation of fuel, while the other electrode, the cathode, promotes electrochemical reduction of an oxidant. Ions generated during oxidation or reduction at the electrodes are transported from one electrode to the other through the ionically conductive electrolyte. The electrolyte medium also serves as a barrier between the fuel and the oxidant. Electrons generated at the anode during the oxidation process pass through the external circuit, whereby electricity is generated, on their way to the cathode, where they complete the reduction reaction. The fuel and oxidant do not mix at any point, and no actual combustion occurs. Fuel cells are classified according to the electrolyte material. The choice of electrolyte material also governs the operating temperature of the fuel cell as well as the nature of the oxidation and reduction reaction.

Polymer electrolyte membrane (PEM) fuel cells (also called proton exchange membrane fuel cells) deliver high-power density and offer advantages of low weight and volume as compared with other fuel cells. PEM fuel cells use a solid polymer as an electrolyte medium and porous carbon electrodes containing a platinum catalyst. They need only hydrogen, oxygen and water to operate and do not require corrosive fluids like some fuel cells. PEM fuel cells operate at relatively low temperatures, typically around 80°C, or at temperatures up to 200°C (high temperature PEM fuel cells). Low-temperature operation allows them to start quickly (less warm up time) and results in less wear on system components, resulting in better durability. PEM fuel cells require that a noble-metal catalyst (typically platinum) be used to separate the hydrogen's electrons and protons, adding to system costs.

An important issue for fuel cells is the poor kinetics of the oxygen reduction reaction (ORR). Even with use of high loadings of expensive noble metal catalysts such as platinum in the electrode, the activation overpotential for the ORR is in the order of 500 mV at acceptable current densities.

In order to improve the performance of the fuel cells, the use of highly active catalysts is essential. Therefore, platinum is widely used because of its high catalytic activity. With the aim of improving the catalytic activity, research and development have been undertaken to increase the surface area of the catalyst metal, i.e. to highly disperse a catalyst metal into small nanoparticles. These small catalyst metal nanoparticles are then loaded on a conductive support.

In the work of developing these new catalyst materials at least two problems have appeared: the so-called particle size effect of platinum for the oxygen reaction and agglomeration.

The particle size effect is disclosed in more details in K.J.J. Mayrhofer et al.; Journal of Physical Chemistry B 109 14433-14440 (2005). The particle size effect is a phenomenon that basically describes that the observed oxygen reduction rates per platinum surface area (turn over frequency) are around 4 times lower on carbon supported platinum nanoparticles having a particle size in the range of 1-5 nm as compared with polycrystalline (bulk) platinum. This phenomenon is not yet understood, but it is believed to be a result of a structure-activity relationship of the ORR on platinum, which is different for highly dispersed platinum particles compared to platinum bulk surfaces. Hence, the common method of employing small supported platinum nanoparticles to maximize the surface area of the catalysts is counterbalanced by this detrimental particle size effect.

Agglomeration is the phenomenon where the spacing between the metal nanoparticles becomes so small that the particles aggregate. Typically, this problem becomes more and more pronounced as the loading amount of the metal nanoparticles is increased.

European patent application EP0325567 is concerned with the problem of obtaining an electrocatalyst material, which is capable of obtaining higher activity for oxygen reduction. The document teaches that although the effect of the activity elevation by

reduction of particle size of the active metal is expected to be elevated as the particle size becomes smaller, a certain limit in fact exists and the mass activity is known to be adversely lowered when the surface area of the active metal is further increased beyond a certain value. In the experimental part it is found that the activity per unit surface area of the platinum gradually increases with the increase of the interparticle distance and the activity reaches a maximum value of about 17 nm in case of the oxygen reduction reaction and 20 nm in case of the air reduction reaction.

European patent application EP1769846 is directed to a metal catalyst containing fine metal particles having a particle diameter of 3 nm or less, which are supported on the surface of carrier particles. It is stated that the distance between centers of adjacent fine particles is preferably less than 15 nm. If the distance is more than 15 nm, the catalytic activity of the metal catalyst may decrease because a supported amount of the fine particles is too small. The distance between neighbour surfaces of adjacent fine metal particles is preferably 0.3 nm or more, because when the distance is less than 0.3 nm, clustering may occur. Moreover, the percentage of the weight of fine metal particles to the weight of the metal catalyst is preferably in the range from 10-60% by weight. When the amount exceeds 60% by weight, the distance between adjacent fine metal particles is less than the above range (i.e. less than 0.3 nm) and clustering may occur.

The inventors of the present invention have surprisingly found that one way to overcome these problems is to densely pack the small platinum nanoparticles on the support material. By such densely packing the particle size effect can be overcome without diminishing the platinum surface area. The inventors of the present invention have found that with 2 nm sized platinum nanoparticles and either a EC300 Ketjen carbon black support of 720 $m^2 g^{-1}$ BET or a EC300J Ketjen carbon black support of approximately 800 $m^2 g^{-1}$ BET or a Vulcan XC-72R support of 235 $m^2 g^{-1}$ BET (Brunauer, Emmett and Teller method) surface area in a range of platinum loadings around 90 wt% platinum (i.e. 90 wt% Pt and 10 wt% carbon) an oxygen reduction rate similar to bulk platinum can be obtained without negatively affecting the platinum area. Furthermore, the inventors have observed indications that the same efficient catalyst can be obtained with even smaller platinum particles. In fact, the inventors work has revealed that the platinum particle coverage, and hence the interparticle distance,

decisively influences the catalytic activity and that densely packed, yet still separated, platinum particles approach platinum bulk activity.

The invention is particular useful when the catalyst material is incorporated in polymer membrane fuel cells, because thinner catalyst layers can be used in the membrane electrode assembly possessing improved performance as compared to commercial cathode layers.

Summary of invention

One aspect of the present invention is to provide a novel catalyst material with an improved specific activity for electrochemical reduction reactions.

Another aspect of the present invention is directed to the use of the novel catalyst material as part of a cathode material in a fuel cell.

Yet another aspect of the present invention is to provide a low temperature fuel cell, such as for example a polymer electrolyte fuel cell comprising the novel catalyst material as a part of the cathode material.

Description of Drawings

Figure 1 shows the reaction rate per platinum surface area (specific activity (SA)) for the oxygen reduction reaction (ORR) at 0.9 V_{RHE} as a function of the catalysts loading, i.e. amount of platinum on carbon support using Pt particles of 2 nm in diameter and a EC 300 Ketjen black high surface area carbon support.

Figure 2 shows the reaction rate per gram platinum (mass activity (MA)) for the oxygen reduction reaction (ORR) at 0.9 V_{RHE} as a function of the catalysts loading. Catalyst: Pt nanoparticles of 2 nm in diameter supported on a EC 300 Ketjen black high surface area carbon support.

Figure 3 shows the Roughness factor (corresponding to the platinum surface area) of the samples as a function of the catalysts loading. The data shows that below 80wt % no agglomeration of the platinum nanoparticles occurs during the electrochemical characterization. Catalyst: Pt nanoparticles of 2 nm in diameter supported on a EC 300 Ketjen black high surface area carbon support.

Figure 4 shows the SA at 0.9 V_{RHE} as a function of the platinum interparticle distance calculated from the catalysts loading. Catalyst: Pt nanoparticles of 2 nm in diameter supported on a EC 300 Ketjen black high surface area carbon support.

Figure 5 shows the reaction rate per platinum surface area (specific activity (SA)) for the oxygen reduction reaction (ORR) at 0.85 V_{RHE} as a function of the edge to edge interparticle distance for Pt particles of 2 nm, 0.8 nm and 0.6 nm in diameter supported on a planar film of amorphous carbon.

Figure 6 shows the reaction rate per Pt surface area (specific activity (SA)) for the oxygen reduction reaction (ORR) as a function of the interparticle distance (edge to edge). The supports are conventional high surface area carbon (Ketjen Black EC 300J and Vulcan XC-72R). The catalyst particles are Pt and PtCo. In all cases the SA increases with decreasing interparticle distance.

Figure 7 shows the ECSA (Pt surface area) of the samples as a function of interparticle distance (edge to edge). The data shows that it is possible to synthesize extremely close lying particles without agglomeration. We think that this could maybe be even further optimized.

Figure 8 shows summarizes the oxygen reduction reaction activities per surface area and per Pt mass (SA and MA) and the ECSA for Pt on Ketjen Black EC 300J.

Figure 9 shows the oxygen reduction reaction activities per surface area and per Pt mass (SA and MA) and the ECSA for Pt on Vulcan XC-72R.

Figure 10 shows the oxygen reduction reaction activities per surface area and per Pt mass (SA and MA) and the ECSA for PtCo on Ketjen Black EC 300J.

Figure 11 shows the stability of the highly loaded (small interparticle distance) catalysts. The graph shows the ECSA loss of Pt/ EC 300J and Pt/ Vulcan XC-72R after 15h of simulated start/stop cycle treatment (potential cycling between 1 and 1.5V_{RHE} with a sweep rate of 500mVs^{-1}, see FCCJ (Fuel Cell Commercialization Conference of

Japan) recommendations in A. Ohma, K. Shinohara, A. Iiyama, T. Yoshida, A. Daimaru, ECS Transactions, 41 (2011) 775-784).

Figure 12 shows the stability of the highly loaded (small interparticle distance) catalysts. The graph shows the ECSA loss of Pt/ EC 300J and Pt/ Vulcan XC-72R after 15h of simulated load cycle treatment (applying square-wave potential steps between 0.6 and 1.0V_{RHE} with a rest time of three seconds at each potential, see FCCJ (Fuel Cell Commercialization Conference of Japan) recommendations in A. Ohma, K. Shinohara, A. Iiyama, T. Yoshida, A. Daimaru, ECS Transactions, 41 (2011) 775-784).

Detailed description of the invention

The present invention is directed to a novel catalyst material comprising metal nanoparticles and a conductive support material, wherein the interparticle distance between the metal nanoparticles is 13 nm or less, and where the metal nanoparticle loading is in the range of 50-90 wt% metal nanoparticles based on the total weight of the catalyst material.

As used herein the term “interparticle distance” (idp) is defined as the average distance between the centre of a catalyst particle and the centre of its nearest neighbouring catalyst particle given by:

$$ipd = \sqrt{\frac{A}{N}}$$

with A being the surface area of the support and N being the number of particles on the support. The interparticle distance therefore depends on the surface area of the catalyst support and is measured as specified below in an example.

As used herein the term “interparticle distance (edge to edge)” (idp_ee) is defined as the average distance between the edge of a catalyst particle and the edge of its nearest neighbouring catalyst particle given by:

$ipd_ee = ipd - d$

with d being the diameter of the catalyst particles on the support.

In some embodiments the interparticle distance is 13 nm or less, such as 12 nm or less, such as 11 nm or less, such as 10 nm or less, such as 9 nm or less, such as 8 nm or less, such as 7 nm or less, such as 6 nm or less such as 5 nm or less. In some embodiments the interparticle distance lies in the range of 1 to 13 nm, such as 1 to 12 nm, such as 1 to 11 nm, such as 1 to 10 nm.

In some embodiments the catalyst material is Pt and the interparticle distance is 13 nm or less, such as 12 nm or less, such as 11 nm or less, such as 10 nm or less, such as 9 nm or less, such as 8 nm or less, such as 7 nm or less, such as 6 nm or less such as 5 nm or less. In some embodiments the interparticle distance lies in the range of 1 to 13 nm, such as 1 to 12 nm, such as 1 to 11 nm, such as 1 to 10 nm. In other embodiments the interparticle distance lies in the range of 2 to 9 nm, such as 2 to 7 nm, such as 2 to 6 nm, such as 2 to 5 nm, such 2 to 4 nm, such as 2 to 3 nm.

In some embodiments the interparticle distance (edge to edge) is 11 nm or less, such as 10 nm or less, such as 9 nm or less, such as 8 nm or less, such as 7 nm or less, such as 6 nm or less, such as 5 nm or less, such as 4 nm or less such as 3 nm or less. In some embodiments the interparticle distance (edge to edge) lies in the range of 0.1 to 11 nm, such as 0.1 to 10 nm, such as 0.1 to 9 nm, such as 0.1 to 8 nm.

In some embodiments the catalyst material is Pt and the interparticle distance (edge to edge) is 11 nm or less, such as 10 nm or less, such as 9 nm or less, such as 8 nm or less, such as 7 nm or less, such as 6 nm or less, such as 5 nm or less, such as 4 nm or less such as 3 nm or less. In some embodiments the interparticle distance (edge to edge) lies in the range of 0.1 to 11 nm, such as 0.1 to 10 nm, such as 0.1 to 9 nm, such as 0.1 to 8 nm. In other embodiments the interparticle distance (edge to edge) lies in the range of 0.5 to 7 nm, such as 0.5 to 6 nm, such as 0.5 to 5 nm, such as 0.5 to 4, such as 0.5 to 3, such as 0.5 to 2.

The metal nanoparticles of the catalyst material of the present invention typically have a diameter of 1 nm or larger. In one embodiment the diameter of the metal nanoparticles lie in the range of from 1 to 20 nm, such as for example 1 to 15 nm, more preferred in the range of 1 to 10 nm, most preferred in the range of 1 to 6 nm.

The catalyst material may be manufactured by any method well-known by a skilled person. Examples are incipient wetness, precipitation and colloidal methods. Typically the catalyst material is manufactured by a colloidal method.

The catalyst material of the present invention comprises metal nanoparticles, which are made of a material selected from the group consisting of Pt, Cr, Ti, V, Fe, Co, Ni, Cu, Zn, Zr, Nb, Ru, Rh, Pd, Ag, In, Sn, Ta, W, Re, Os, Ir and Au, or the material may be selected from the group of platinum alloys, which includes all alloys of Pt with the elements Cr, Ti, V, Fe, Co, Ni, Cu, Zn, Zr, Nb, Ru, Rh, Pd, Ag, In, Sn, Ta, W, Re, Os, Ir, Y, Sc, La and Au. In another embodiment the material may be selected from the group of platinum alloys, which includes all alloys of Pt with the elements Cr, Ti, V, Fe, Co, Ni, Cu, Zn, Zr, Nb, Ru, Rh, Pd, Ag, In, Sn, Ta, W, Re, Os, Ir, Y, Sc, La, Gd and Au. Preferably the metal nanoparticles are made of platinum or platinum alloys, most preferred Pt, PtCo, PtNi, PtCu, PtFe, PtAu, and PtCr. In one embodiment the catalyst material is not made of Ru. In one embodiment the catalyst material is not made of a platinum alloy, which includes Pt and Ru.

The conductive support of the novel catalyst material may be any conductive support known within the art. Preferably the conductive support is selected from the group consisting of carbon, Pt, Ti, V, Fe, Co, Ni, Cu, Zn, Zr, Nb, Ru, Rh, Pd, Ag, In, Sn, Ta, W, Re, Os, Ir and Au, as well as their oxides and their carbides. In a preferred embodiment the conductive support is made of carbon, such as for example EC300J Ketjen Black, EC600 JD Ketjen black, Black Pearls BP2000, Vulcan XC-72 and graphitized versions thereof.

The major advantage of the catalyst material of the present invention is that a high nanoparticle loading is obtainable without negatively affecting the surface reactivity. By the term nanoparticle loading as used herein is meant the amount of metal particles that may be loaded on the conductive support and is expressed in weight of metal nanoparticles per total weight of catalyst material. Preferably, the metal nanoparticle loading is in the range of 50-90 wt% metal nanoparticles based on the total weight of the catalyst material, such as for example in the range of 60-90 wt%, such as 70-90 wt%, such as for example 50-85 wt%, such as 60-85 wt%, such as 70-85 wt%, such as 80-85wt %, such as for example 50-80 wt%, such as 60-80 wt%, such as 70-80 wt%.

A skilled person would recognize that the nanoparticle loading will depend on the nature of the metal particles and conductive support, especially on the density of the metal particles and conductive material.

Hence in a very preferred embodiment, where the metal nanoparticles are made of platinum and the conductive support is made of carbon, the platinum loading is in the range of 50-90 wt% platinum nanoparticles based on the total weight of the catalyst material, such as for example in the range of 60-90 wt%, such as 70-90 wt%, such as for example 50-85 wt%, such as 60-85 wt%, such as 70-85 wt%, such as 80-85wt %, such as for example 50-80 wt%, such as 60-80 wt%, such as 70-80 wt%. Preferably the platinum loading is 70 wt%.

In other preferred embodiments, where the metal nanoparticles are made of an alloy of platinum and another element and the conductive support is made of carbon, the metal alloy loading is in the range of 50-90 wt% metal alloy nanoparticles based on the total weight of the catalyst material, such as for example in the range of 50-80 wt%, such as 50-70 wt%, such as for example 50-60 wt%, such as 60-70 wt%, such as 55-65 wt%, such as 55-70wt %, such as for example 60-75 wt%, such as 60-65 wt%.

In principle the novel catalyst material of the present invention may be used in catalysing many different reactions. However, preferably the catalyst material is used for catalysing electrochemical processes, such as hydrogen oxidation, oxygen evolution, most preferable electrochemical reduction processes, such as carbon dioxide reduction or the oxygen reduction reaction, which takes place in a fuel cell. The fuel cell may be any kind of fuel cell, where the cathode reaction is the reduction of oxygen, but preferably the fuel cell is a low to intermediate temperature fuel cell, such as a low temperature polymer electrolyte fuel cell, a high temperature polymer electrolyte fuel cell, an alkaline fuel cell or a phosphoric acid fuel cell.

The present invention is also directed to cathode material, which is made of the novel catalyst material of the present invention. In general, the cathode may take any kind of shape that is known within the art, but the membrane shape is the preferred shape.

The present invention also relates to low to intermediate temperature (below 300C) fuel cells comprising a cathode material made of or comprising the catalyst material of the

present invention. Preferably, the low to intermediate temperature fuel cell is a low temperature polymer electrolyte fuel cell, a high temperature polymer electrolyte fuel cell, an alkaline fuel cell or a phosphoric acid fuel cell.

Electrochemical Characterization of the catalyst material

Electrochemical measurements were performed in a Teflon cell with three compartments using a computer controlled potentiostat and a rotating disk electrode (RDE) setup. The counter (auxiliary) electrode was a platinum wire, and a Schott Kalomel (B 2810) served as reference electrode which was placed in an ion membrane (Nafion) separated compartment filled with suprapur 0.1 M $HClO_4$. This membrane serves to avoid the diffusion of Cl^- into the test solution [K.J.J. Mayrhofer, S.J. Ashton, J. Kreuzer, M. Arenz, Int. J. Electrochem. Sci., 4 (2009) 1-8]. All potentials in this work are referred to the reversible hydrogen electrode (RHE) potential, which was experimentally determined for each measurement series. All solutions were prepared in Millipore® water (>18.3 MΩ cm, TOC < 5 ppb). $HClO_4$ and HCl acids were from Merck (suprapur) and all Measurements were performed at 20°C.

Prior to the oxygen reduction reaction (ORR) measurements the glassy carbon (GC) working electrodes (5 mm diameter, 0.196 cm^2 geometrical surface area) were polished to mirror finish with alumina oxide paste 0.3 and 0.05 µm (Buelher-Met, deagglomerated α-alumina and γ-alumina, respectively), and cleaned ultrasonically in ultrapur water and cc. 70% $HClO_4$. The catalyst ink was prepared by ultrasonically dispersing the catalyst powder in ultrapure water (0.14 mg_{Pt} mL^{-1}). A volume of 20 µL of the suspension was then placed onto a polished and cleaned glassy carbon substrate leading to a Pt loading (M_L) of 14 μg_{Pt} cm^{-2} for the catalyst sample. The catalyst suspension was dried onto the glassy carbon electrode in a nitrogen gas stream. The experiments were performed in 0.1M $HClO_4$ solutions. Initially, the electrolyte was de-aerated by purging with Ar gas (99.998%, Air Liquide), and the surface of the catalyst was cleaned by potential cycles between 0.05 and 1.1 V *vs.* reversible hydrogen electrode (RHE) at a scan rate of 50 mVs^{-1}.

The specific activity (SA) of the ORR is calculated from the positive going RDE polarization curves recorded at a scan rate of 50 mV s^{-1} using a rotation rate of 1600 rpm [M. Nesselberger, S. Ashton, J.C. Meier, I. Katsounaros, K.J.J. Mayrhofer, M. Arenz, J. Am. Chem. Soc., 133 (2011) 17428-174332]. As overall activity the kinetic

current j_k per geometric GC surface area is determined by:

$$j_k = \frac{j_{d,RDE}\, j}{j_{d,RDE} - j}$$

With j measured current at $0.9V_{RHE}$, and $j_{d,RDE}$ diffusion limited current. The polarization curves are corrected for the non-faradaic background by subtracting the cyclovoltammograms (CVs) recorded in Ar-purged electrolyte. The IR-drop the solution resistance between the working electrode and the Luggin capillary was compensated. The resulting effective solution resistance was less than 3 Ω for each experiment. The electrochemical surface areas (ECSA) of the catalysts are calculated from the so-called CO stripping charge [M. Nesselberger, S. Ashton, J.C. Meier, I. Katsounaros, K.J.J. Mayrhofer, M. Arenz, J. Am. Chem. Soc., 133 (2011) 17428-174332]: CO is adsorbed at a potential of $50mV_{RHE}$ until saturation is reached and then removed from the electrolyte solution by purging with Ar. Then a positive going polarization curve is recorded oxidizing all CO.

For calculating roughness factor R_f the current density under the oxidation peak is integrated leading to Q_{CO} in units of C/cm^2 and normalized (divided by) to the value of 420 $\mu C\ cm^{-2}$ for polycrystalline Pt.

$$R_f = \frac{Q_{CO}}{420\frac{\mu C}{cm^2}} \qquad Q_{CO} = \frac{\int j\, dE}{dE/dt} = \int j\, dt$$

With E = E (t) as the working electrode potential and t as time. The ECSA is calculated by dividing the roughness factor and platinum loading.

$$ECSA = \frac{R_f}{M_L}$$

The specific activity (SA) and mass activity (MA) are determined by

$$SA = \frac{j_k}{R_f} \qquad MA = SA \times ECSA$$

Calculation of the interparticle distance

As interparticle distance (idp) we define the average distance between the centre of a catalyst particle and the centre of its nearest neighbouring catalyst particle given by:

$$ipd = \sqrt{\frac{A}{N}}$$

For the specific case of synthesizing the catalyst using a colloidal method of Pt nanoparticles, the interparticle distance is calculated based on the BET surface area of the support and the average particle size of the Pt nanoparticles established in TEM and SAXS. The theoretical interparticle distance is experimentally confirmed by TEM.

The interparticle distance ipd_{Pt} is for this example calculated according to the below formula

$$ipd_{Pt} = \sqrt{\frac{\mathrm{A_C}}{N_{Pt}}} = \sqrt{\frac{\mathrm{A_C}}{\mathrm{V_{sus}} \cdot n_{Pt}}} = \sqrt{\frac{\mathrm{A_C}}{\mathrm{V_{sus}}} \frac{\frac{1}{6}\pi d^3 \varrho}{c_{Pt}}} = \sqrt{\frac{\mathrm{a_C} \cdot \mathrm{M_C}}{\mathrm{V_{sus}}} \frac{\frac{1}{6}\pi d^3 \varrho}{c_{Pt}}}$$

where

N_{Pt}: The absolute number of Pt particles mixed with the carbon support

A_C is the absolute BET surface area of the support; unit m^2;

n_{Pt} : number of Pt particles per liter Aceton; unit l^{-1}

V_{sus}: Volume of Pt/Aceton suspension mixed with carbon support; unit l

c_{Pt} : Pt concentration in colloidal Pt/Aceton suspension; unit $g_{Pt}\, l^{-1}$

d: average Pt particle diameter; unit nm

ϱ: Pt density; unit g nm^{-3} ($21.45\ 10^{-21}$ g·m^{-3})

a_C : specific BET area of carbon support; unit $m^2\, g^{-1}$

M_C: amount of carbon mixed with Pt/Aceton suspension; unit g

Single calculation steps:

Volume of one Pt particle: $\frac{1}{6}\pi d^3$

Mass of one Pt particle: $\frac{1}{6}\pi d^3 \varrho$

$$n_{Pt} = \frac{c_{Pt}}{\frac{1}{6}\pi d^3 \varrho}$$

$$N_{Pt} = n_{Pt} \cdot \mathrm{V_{sus}}$$

$$\mathrm{A_C} = \mathrm{a_C} \cdot \mathrm{M_C}$$

Calculation example 1:

Calculation of the interparticle distance of a catalyst based on a colloidal Pt/Aceton suspension with a Pt concentration of c_{Pt} = 8 g/l, of which 2 ml are mixed with 4mg EC300 carbon support.

a_{EC300} = 720 m^2g^{-1}

A_{EC300} = 720·m^2g^{-1} · 4·10^{-3}g = 2.88 m^2

The number of Pt particles in 2ml suspension is:

$$N_{Pt} = \frac{c_{Pt}}{\frac{1}{6}\pi d^3 \varrho} \cdot 2\ 10^{-3}\mathrm{l} = \frac{8\frac{\mathrm{g}}{\mathrm{l}}}{\frac{1}{6}\pi(2\ 10^{-9}\mathrm{m})^3 \cdot 21.45\ 10^6\ \mathrm{g}\cdot\mathrm{m}^{-3}} \cdot 2\ 10^{-3}\mathrm{l} = \frac{12\ 10^{-3}}{\pi \cdot 10^{-27} \cdot 21.45 \cdot 10^6} = 1.780\ 10^{17}$$

With d = average Pt particle diameter in nm (2nm); ϱ Pt density in g nm^{-3} (21.45 10^6 g·m^{-3}).

Therefore the average interparticle distance is calculated to

$$ipd_{Pt} = \sqrt{\frac{A_C}{N_{Pt}}} = \sqrt{\frac{2.88\ \mathrm{m}^2}{1.780\ 10^{17}}} = 4.02156\ 10^{-9}\mathrm{m} = 4.02156\ \mathrm{nm}$$

Calculation example 2:

Calculation of the interparticle distance of a catalyst based on a colloidal Pt/Aceton suspension with a Pt concentration of c_{Pt} = 8 g/l, of which 2 ml are mixed with 4mg EC300J carbon support.

a_{EC300J} = 795 m^2g^{-1}

A_{EC300J} = 795·m^2g^{-1} · 4·10^{-3}g = 3.18 m^2

The number of Pt particles in 2ml suspension is:

$$N_{Pt} = \frac{c_{Pt}}{\frac{1}{6}\pi d^3 \varrho} \cdot 2\ 10^{-3}\mathrm{l} = \frac{8\frac{\mathrm{g}}{\mathrm{l}}}{\frac{1}{6}\pi(2\ 10^{-9}\mathrm{m})^3 \cdot 21.45\ 10^6\ \mathrm{g}\cdot\mathrm{m}^{-3}} \cdot 2\ 10^{-3}\mathrm{l} = \frac{12\ 10^{-3}}{\pi \cdot 10^{-27} \cdot 21.45 \cdot 10^6} = 1.780\ 10^{17}$$

With d = average Pt particle diameter in nm (2nm); ϱ Pt density in g nm^{-3} (21.45 10^6 $g \cdot m^{-3}$).

Therefore the average interparticle distance is calculated to

$$ipd_{Pt} = \sqrt{\frac{A_C}{N_{Pt}}} = \sqrt{\frac{3.18\ m^2}{1.780\ 10^{17}}} = 4.227\ 10^{-9}\mathrm{m} = 4.227\ \mathrm{nm}$$

and the average interparticle distance (edge to edge) is

$$4.227\ nm - 2\ nm = 2.227\ nm$$

Examples

Example 1

Pt Particle synthesis

According to the procedure of Wang et al. [Y. Wang, J.W. Ren, K. Deng, L.L. Gui, Y.Q. Tang, Preparation of tractable platinum, rhodium, and ruthenium nanoclusters with small particle size in organic media, Chemistry of Materials, 12 (2000) 1622-1627] 10ml of 0.4 M NaOH/ethylene glycol (NaOH/EG) solution are filled into a 50ml round bottomed flask with magnetic stir bar and reflux condenser. Then in total 10 ml of orange colored H_2PtCl_6/EG solution (8 g/l Pt^{4+}) are drop wise added under stirring. The solution is stirred 15 min. at room temperature and thereafter heated for 3 h at 160 °C under light reflux. Thereafter the solution is cooled to room temperature obtaining 20 ml of a colloidal Pt Nanoparticle (PtNPs) suspension in ethylene glycol with a Pt concentration of 4 g/l.

Preparing supported Pt nanoparticles

In order to support the Pt nanoparticles 4 ml of the 4 g/l Pt/EG suspension are mixed with excess 1 M HCl solution in order to precipitate the nanoparticles. Thereafter the suspension is centrifuged and the Excess discarded. The nanoparticles are then washed 3 times in 1 M HCl solution and thereafter re-suspended in 2 ml of Aceton. Assuming 100% efficiency this leads to a colloidal Pt/Aceton suspension with a Pt concentration of 8 g/l.

The Pt/Aceton suspension (typically 2ml) is then added into a glass vial to a support (typically, but not necessarily, a carbon powder; for example the carbon Ketjen Black EC 300) in a defined Pt/C mass (weight) ratio. This is typically between 20/80 and

90/10 Pt/C weight ratio (For 80/20 weight ratio 2ml suspension containing 16mg Pt are mixed with 4mg support). The mixture is thereafter dried in a ultrasonic bath evaporating the Aceton. The resulting catalyst is analyzed electrochemically as well as by SAXS (small angle X-ray diffraction) and TEM (Transmission electron microscopy).

The average interparticle distance is calculated based on the surface area of the support (measured by the so-called BET (Brunauer, Emmett and Teller) method (fx. 720 m^2/g (BET) for Ketjen Black EC 300) and the average particle size of the PtNPs established in TEM (typically 2nm). The interparticle distance is defined as the average distance between the centre of a catalyst particle and the centre of its nearest neighbouring catalyst particle. The theoretical inter-particle distance is experimentally confirmed by TEM.

Results

Catalyst material was prepared as described above and then subjected to the electrochemical characterization as described above. The results are shown in Table 1 and Figures 1-4.

Table 1:

Pt loading / w%	Roughness factor (Rf)	Specific activity (SA) / $mAcm^{-2}$	Mass activity (MA) / Amg^{-1}_{Pt}	Interparticle distance / nm
2	7,43	0,204	0,108	59,00
5	9,41	0,337	0,227	36,00
10	6,91	0,321	0,158	25,32
20	7,27	0,473	0,245	16,88
30	7,92	0,561	0,318	12,89
40	8,26	0,580	0,342	10,34
50	7,69	0,548	0,301	8,44
60	8,00	0,614	0,351	6,89
65	9,55	0,643	0,438	6,21
72	8,50	0,671	0,408	5,29
80	7,88	0,774	0,436	4,21
82	6,16	0,722	0,317	3,95
84	6,04	0,817	0,352	3,68
90	5,14	0,849	0,312	2,81

Figure 1 shows the reaction rate per Pt surface area (specific activity (SA)) for the oxygen reduction reaction (ORR) as a function of the catalysts loading, i.e. amount of Pt on carbon support. The support is a conventional high surface area carbon (Ketjen Black EC 300). It shows that the SA increases with increasing Pt loading.

Figure 2 shows the reaction rate per gram Pt (mass activity (MA)) for the oxygen reduction reaction (ORR) as a function of the catalysts loading.

Figure 3 shows the Roughness factor (corresponding to the Pt surface area) of the samples as a function of the catalysts loading. The data shows that below 80wt % no agglomeration of the Pt nanoparticles occurs during the electrochemical characterization. We think that this could maybe be even further optimized.

Figure 4 shows the SA as a function of the Pt interparticle distance calculated from the catalysts loading.

Also considerable work has been conducted in the past to understand the relationship between the specific activity and interparticle distance. As a result of this work, Figure 5 shows the reaction rate per platinum surface area (specific activity (SA)) for the oxygen reduction reaction (ORR) at 0.85 V_{RHE} as a function of the edge to edge interparticle distance for Pt particles of 2 nm, 0.8 nm and 0.6 nm in diameter supported on a planar film of amorphous carbon.

Discussion of results

The results shown in Figure 1 indicate that the reaction rate per Pt surface area (specific activity (SA)) for the oxygen reduction reaction linear increases with Pt loading. As at the same time the active surface area (expressed as roughness factor) is constant up to a Pt loading of around 75% (see Figure 3), the reaction rate per gram Pt (mass activity (MA)) for the oxygen reduction reaction exhibits a maximum at a specific Pt loading (see Figure 2). The preferred catalysts exhibit a Pt loading at the point of maximum mass activity. If the size of the Pt particles and the surface area of the support are known and well defined (low standard deviation) one can relate the ideal Pt loading to an interparticle distance (Figure 4), which is the decisive general property as proven in Figure 5. In Table 1 a comparison of the relation between Pt loading, obtained Rf, SA, MA, and the calculated interparticle distance is shown.

Example 2

Pt Particle synthesis

According to the procedure of Wang et al. [Y. Wang, J.W. Ren, K. Deng, L.L. Gui, Y.Q. Tang, Preparation of tractable platinum, rhodium, and ruthenium nanoclusters with small particle size in organic media, Chemistry of Materials, 12 (2000) 1622-1627] 10ml of 0.4 M NaOH/ethylene glycol (NaOH/EG) solution are filled into a 50ml round bottomed flask with magnetic stir bar and reflux condenser. Then in total 10 ml of orange colored H_2PtCl_6/EG solution (8 g/l Pt^{4+}) are drop wise added under stirring. The solution is stirred 15 min. at room temperature and thereafter heated for 3 h at 160 °C under light reflux. Thereafter the solution is cooled to room temperature obtaining 20 ml of a colloidal Pt Nanoparticle (PtNPs) suspension in ethylene glycol with a Pt concentration of 4 g/l.

PtCo Particle synthesis

To obtain PtCo Particles 10ml of 0.4 M NaOH/ethylene glycol (NaOH/EG) solution are filled into a 50ml round bottomed flask with magnetic stir bar and reflux condenser in inert (Argon) atmosphere. Then in total 10 ml of a 1 to 1 mixture of orange colored H_2PtCl_6/EG solution (4 g/l Pt^{4+}) and $CoCl_2 \cdot 6H_2O$/EG (4 g/l Co^{2+}), with or without the addition of hexadecyl trimethyl ammonium bromide (CTAB) as surfactant, are drop wise added under stirring. The solution is stirred 15 min. at room temperature and thereafter heated for 3 h at 160 °C under light reflux. Thereafter the solution is cooled to room temperature obtaining 20 ml of a colloidal Pt:Co Nanoparticle (PtNPs) suspension in ethylene glycol with a metal concentration of 4 g/l.

Preparing supported catalysts from the nanoparticles

In order to support the Pt nanoparticles 4 ml of the 4 g/l Pt/EG suspension are mixed with excess 1 M HCl solution in order to precipitate the nanoparticles. Thereafter the suspension is centrifuged and the Excess discarded. The nanoparticles are then washed 3 times in 1 M HCl solution and thereafter re-suspended in 2 ml of Aceton. Assuming 100% efficiency this leads to a colloidal Pt/Aceton suspension with a Pt concentration of 8 g/l.

The Pt/Aceton suspension (typically 2ml) is then added into a glass vial to a support (typically, but not necessarily, a carbon powder; for example the carbon Ketjen Black

EC 300 or the carbon Vulcan XC-72R) in a defined Pt/C mass (weight) ratio. This is typically between 20/80 and 90/10 Pt/C weight ratio (For 80/20 weight ratio 2ml suspension containing 16mg Pt are mixed with 4mg support). The mixture is thereafter dried in a ultrasonic bath evaporating the Aceton. The resulting catalyst is analyzed electrochemically as well as by SAXS (small angle X-ray diffraction) and TEM (Transmission electron microscopy).

In order to support the Pt:Co nanoparticles 4 ml of the 4 g/l Pt:Co/EG suspension are mixed with excess 1 M HCl solution or pure Isopropanol in order to precipitate the nanoparticles. Thereafter the suspension is centrifuged and the Excess discarded. The nanoparticles are then washed 3 times in 1 M HCl solution or Isopropanol and thereafter re-suspended in 2 ml of Aceton. Assuming 100% efficiency this leads to a colloidal Pt:Co/Aceton suspension with a metal concentration of 8 g/l and a Pt concentration of 4 g/l.

The Pt:Co /Aceton suspension (typically 2ml) is then added into a glass vial to a support (typically, but not necessarily, a carbon powder; for example the carbon Ketjen Black EC 300) in a defined Pt/C mass (weight) ratio. This is typically between 20/80 and 90/10 Pt/C weight ratio (For 60/40 Pt/C weight ratio 1.5ml suspension containing 6mg Pt are mixed with 4mg support). The mixture is thereafter dried in a ultrasonic bath evaporating the Aceton. The resulting catalyst is analyzed electrochemically as well as by SAXS (small angle X-ray diffraction) and TEM (Transmission electron microscopy).

The average interparticle distance is calculated based on the surface area of the support (measured by the so-called BET (Brunauer, Emmett and Teller) method (fx. 795 m^2/g (BET) for Ketjen Black EC 300 and 235 m^2/g (BET) for Vulcan XC-72R) and the average particle size of the Pt NPs or Pt:Co NPs established in TEM (typically 2nm). The interparticle distance is defined as the average distance between the centre of a catalyst particle and the centre of its nearest neighbouring catalyst particle. The theoretical inter-particle distance is experimentally confirmed by TEM.

Results

Catalyst material was prepared as described above and then subjected to the electrochemical characterization as described above. The results are shown in Tables 2-4 and Figures 6-12.

Table 2:

Carbon support Ketjen Black EC 300 with surface area 795 m^2/g (BET); Pt nanoparticles with 2 nm diameter.

Pt loading [wt. % Pt]	ECSA [$m^2 g_{Pt}^{-1}$]	Specific activity [$mA\ cm^{-2}$]	Mass activity [$A\ g^{-1}_{Pt}$]	Interparticle distance [nm]	
				Center to Center	Edge to Edge
2	53.30	0.204	108	59.15	57.15
5	67.51	0.337	227	36.83	34.83
10	49.57	0.321	158	25.35	23.35
20	52.15	0.473	245	16.90	14.90
30	56.82	0.561	318	12.91	10.91
40	59.26	0.580	342	10.35	8.35
50	55.17	0.548	301	8.45	6.45
60	57.39	0.614	351	6.90	4.90
65	68.51	0.643	438	6.20	4.20
72	60.98	0.671	408	5.27	3.27
80	56.53	0.774	436	4.22	2.22
82	44.19	0.722	317	3.96	1.96
84	43.33	0.817	352	3.69	1.69
90	36.87	0.849	312	2.82	0.82

Table 3:

Carbon support Vulcan XC-72R with surface area 235 m^2/g (BET); Pt nanoparticles with 1,7 nm diameter.

Pt loading [wt. % Pt]	ECSA [$m^2 g_{Pt}^{-1}$]	Specific activity [$mA\ cm^{-2}$]	Mass activity [$A\ g^{-1}_{Pt}$]	Interparticle distance [nm]	
				Center to Center	Edge to Edge
30	100.15	0.441	442	7.02	5.02
60	97.21	0.573	557	3.75	1.75
70	93.05	0.735	684	3.01	1.01
80	72.67	0.978	711	2.30	0.30

Table 4:

Carbon support Ketjen Black EC 300J with surface area 795 m^2/g (BET); PtCo nanoparticles with 2.1 nm diameter.

Pt loading [wt. % Pt]	ECSA [$m^2 g_{Pt}^{-1}$]	Specific activity [$mA\ cm^{-2}$]	Mass activity [$A\ g^{-1}_{Pt}$]	Interparticle distance [nm]	
				Center to Center	Edge to Edge
20	56.14	0.668	375	19.50	17.30
30	63.63	0.730	464	14.89	12.69
40	53.30	0.715	381	11.94	9.74
60	60.33	0.863	521	7.96	5.76
70	49.71	1.018	506	6.38	4.18
80	39.09	1.280	500	4.87	2.67

Discussion of results

The results summarized in Figure 6 show that the inventive idea can be applied to different supports, i.e. the specific activity for the oxygen reduction reaction of a catalyst depends on the interparticle distance as well as particle composition. In general it can be stated that Pt alloys exhibit an improved specific and mass activity as compared to pure Pt nanoparticles. This is demonstrated for the example of PtCo in Fig. 6 (SA) and comparing Figs. 8, 9, and 10 (MA).

However it has to be considered that the ECSA might depend on the type of the used support because the particle sticking is support dependent. This is demonstrated in Fig. 7. Finally we demonstrate in Figs. 11 and 12 that catalysts with low interparticle distance not only exhibit improved activity, but also improved stability. For this purpose we applied two accelerated stress tests (AST) treatments, recommended by the Fuel Cell Commercialization Conference of Japan (FCCJ) published in Ohma et al, *ECS Transactions*, 2011, **41**, 775-784.

Claims

1. A catalyst material comprising metal nanoparticles and a conductive support material, wherein the interparticle distance between the metal nanoparticles is 13 nm or less, and where the metal nanoparticle loading is in the range of 50-90 wt% metal nanoparticles based on the total weight of the catalyst material.

2. The catalyst material according to claim 1, wherein the metal nanoparticles have a diameter of 1 nm or larger.

3. The catalyst material according to any of the preceding claims, wherein the interparticle distance (edge to edge) is 11 nm or less.

4. The catalyst material according to any of the preceding claims, wherein the metal nanoparticles are made of a material selected from Pt and the group of platinum alloys, which includes all alloys of Pt with the elements Cr, Ti, V, Fe, Co, Ni, Cu, Zn, Zr, Nb, Ru, Rh, Pd, Ag, In, Sn, Ta, W, Re, Os, Ir, Y, Sc, La and Au.

5. The catalyst material according to any of the preceding claims, wherein the conductive support is selected from the group consisting of carbon, Pt, Ti, V, Fe, Co, Ni, Cu, Zn, Zr, Nb, Ru, Rh, Pd, Ag, In, Sn, Ta, W, Re, Os, Ir and Au, as well as their oxides and their carbides.

6. The catalyst material according to any of the preceding claims, wherein the metal nanoparticles are made of platinum and the conductive support is made of carbon and the platinum loading is in the range of 50-90 wt% platinum nanoparticles based on the total weight of the catalyst material.

7. The catalyst material according to any of the preceding claims, wherein the metal nanoparticles are made of platinum alloys and the conductive support is made of carbon and the platinum alloy loading is in the range of 50-70 wt% platinum alloy nanoparticles based on the total weight of the catalyst material.

8. Use of the catalyst material according to any of the preceding claims in a fuel cell.

9. Use according to claim 8, wherein the fuel cell is a low temperature fuel cell, such as a polymer electrolyte fuel cell.

10. Cathode material made of the catalyst material according to any of claims 1-7.

11. Low temperature fuel cell comprising a cathode made of the catalyst material according to any of claims 1-7.

12 The low temperature fuel cell according to claim 11, wherein the low temperature fuel cell is a polymer electrolyte fuel cell.

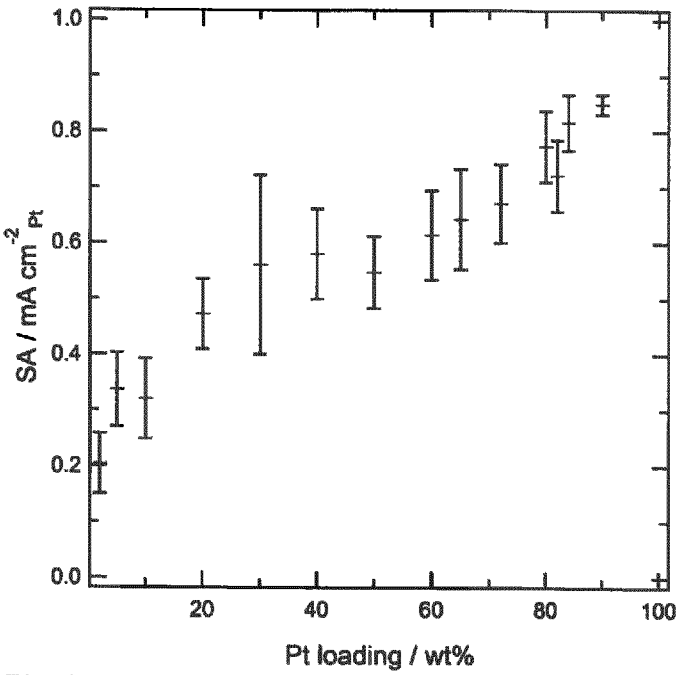

SA / mA cm$^{-2}_{Pt}$
1.0
0.8
0.6
0.4
0.2
0.0
20
40
60
80
100
Pt loading / wt%

Fig. 1

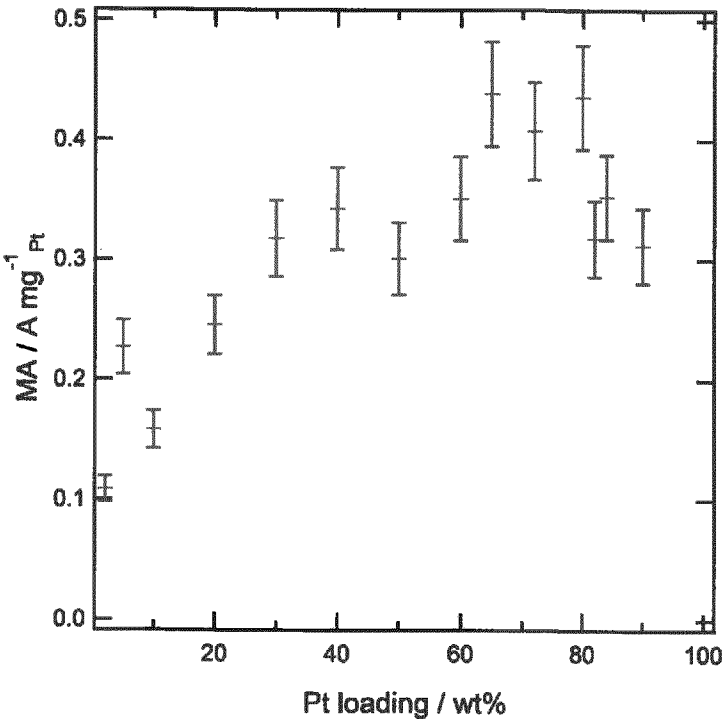

MA / A mg$^{-1}_{Pt}$
0.5
0.4
0.3
0.2
0.1
0.0
20
40
60
80
100
Pt loading / wt%

Fig. 2

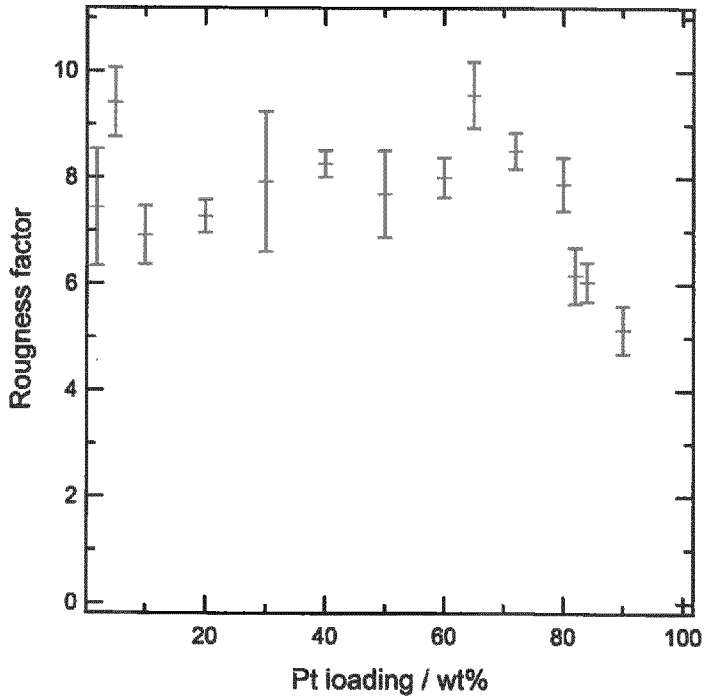

Rougness factor
Pt loading / wt%
0
2
4
6
8
10
20
40
60
80
100

Fig. 3

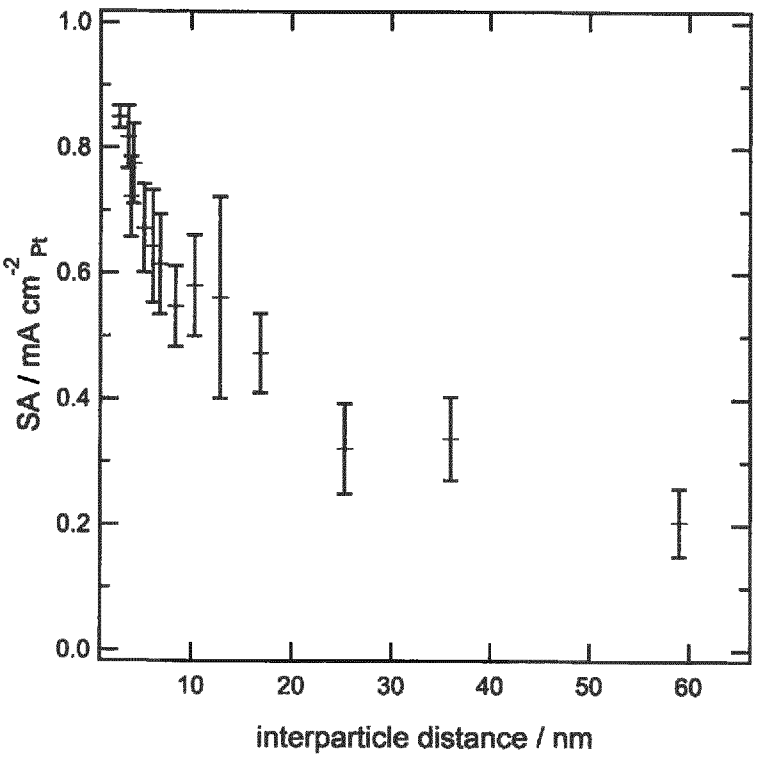

SA / mA cm-2 Pt
interparticle distance / nm
0.0
0.2
0.4
0.6
0.8
1.0
10
20
30
40
50
60

Fig. 4

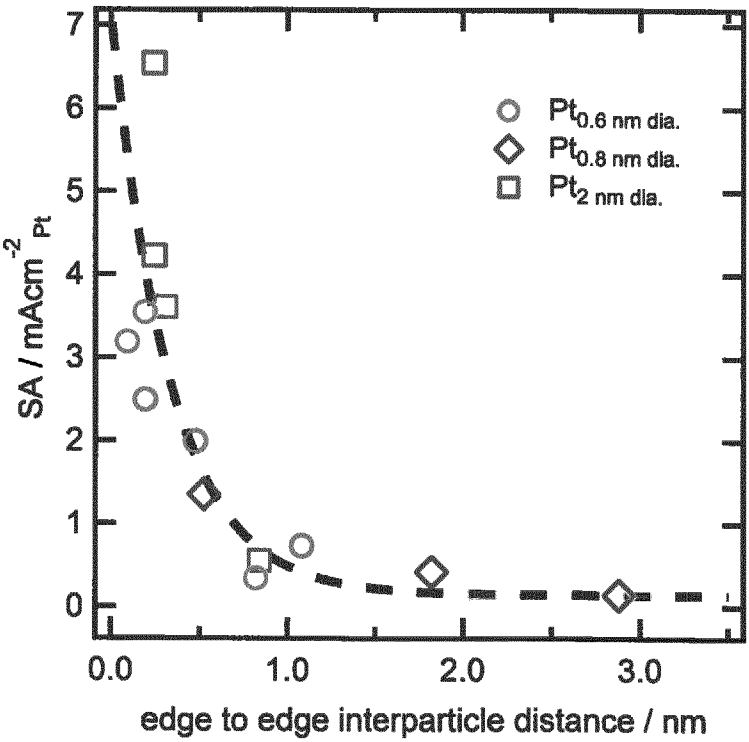

SA / mAcm$^{-2}_{Pt}$
edge to edge interparticle distance / nm
$Pt_{0.6\ nm\ dia.}$
$Pt_{0.8\ nm\ dia.}$
$Pt_{2\ nm\ dia.}$
0
1
2
3
4
5
6
7
0.0
1.0
2.0
3.0

Fig. 5

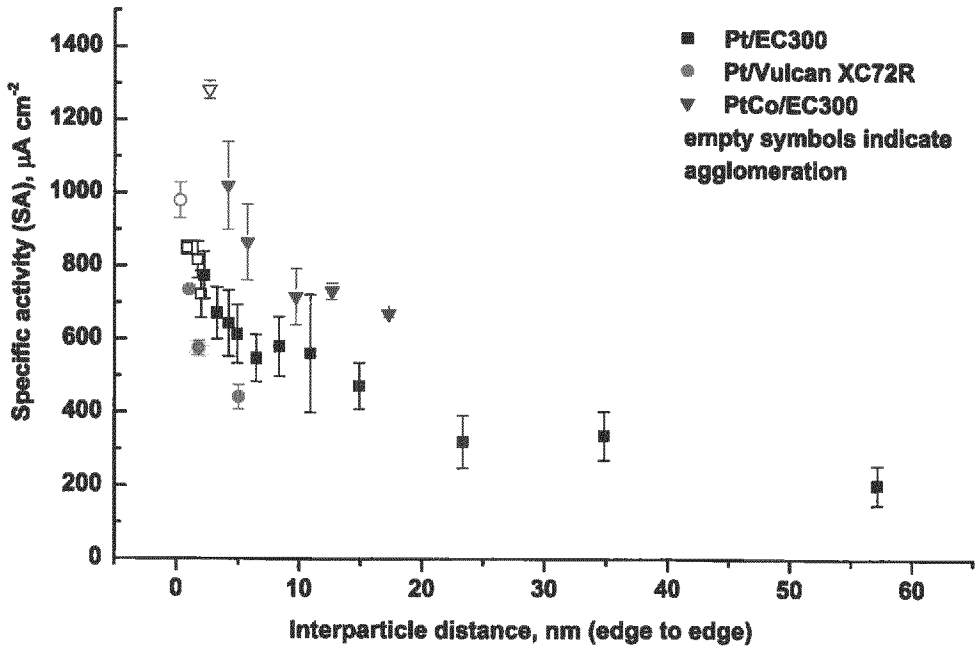

Specific activity (SA), µA cm^{-2}
Interparticle distance, nm (edge to edge)
Pt/EC300
Pt/Vulcan XC72R
PtCo/EC300
empty symbols indicate agglomeration
0
200
400
600
800
1000
1200
1400
0
10
20
30
40
50
60

Fig. 6

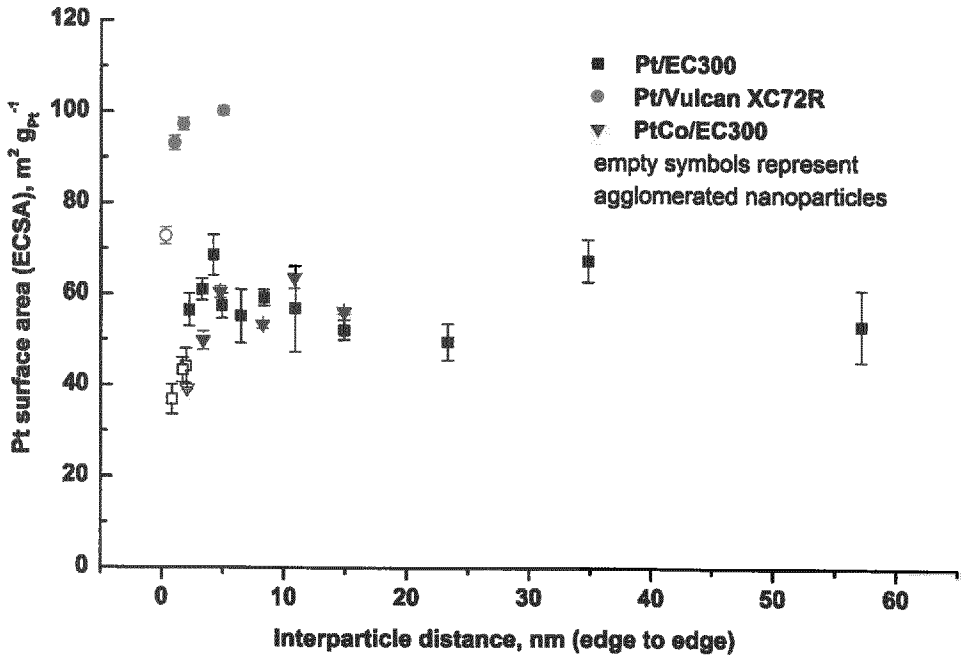

Pt surface area (ECSA), m² g_Pt⁻¹
Interparticle distance, nm (edge to edge)
Pt/EC300
Pt/Vulcan XC72R
PtCo/EC300
empty symbols represent
agglomerated nanoparticles

Fig. 7

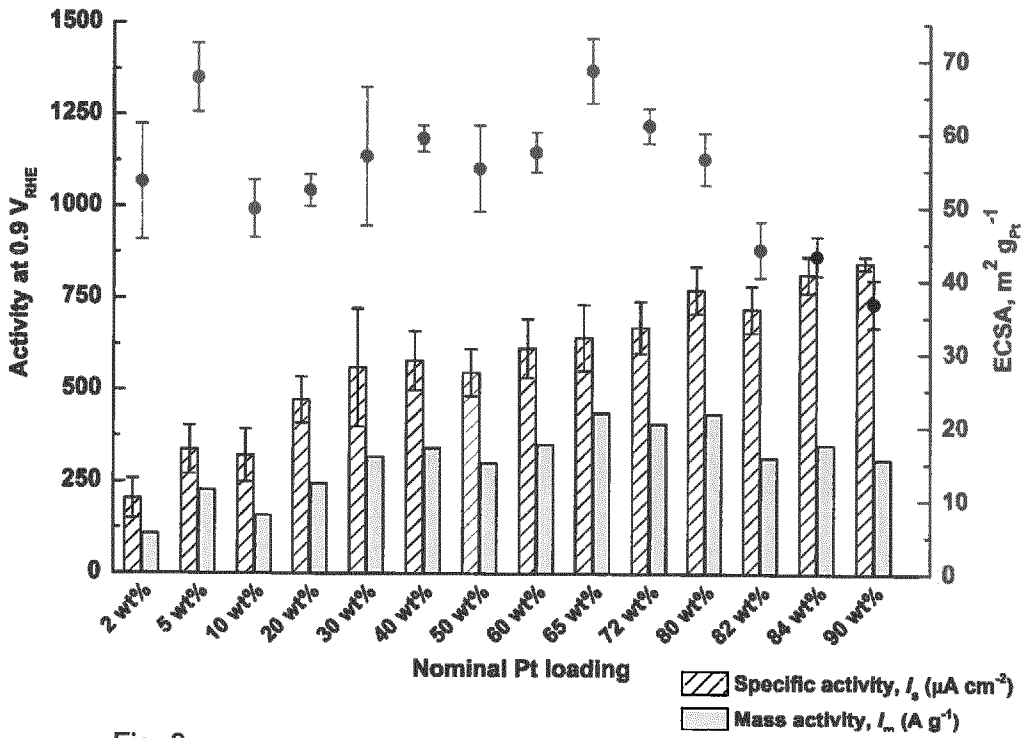

Activity at 0.9 V_RHE
ECSA, m² g_Pt⁻¹
2 wt%
5 wt%
10 wt%
20 wt%
30 wt%
40 wt%
50 wt%
60 wt%
65 wt%
72 wt%
80 wt%
82 wt%
84 wt%
90 wt%
Nominal Pt loading
Specific activity, I_s (μA cm⁻²)
Mass activity, I_m (A g⁻¹)

Fig. 8

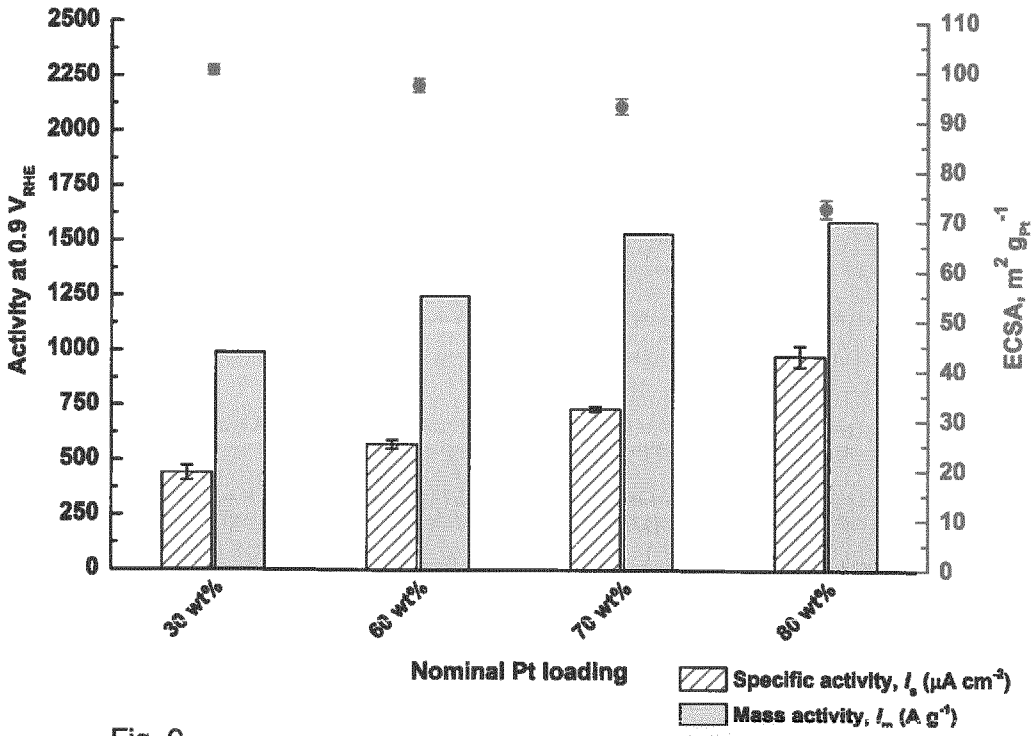

Activity at 0.9 V_{RHE}
ECSA, $m^2 g_{Pt}^{-1}$
2500
2250
2000
1750
1500
1250
1000
750
500
250
0
110
100
90
80
70
60
50
40
30
20
10
0
30 wt%
60 wt%
70 wt%
80 wt%
Nominal Pt loading
Specific activity, I_s (μA cm^{-2})
Mass activity, I_m (A g^{-1})

Fig. 9

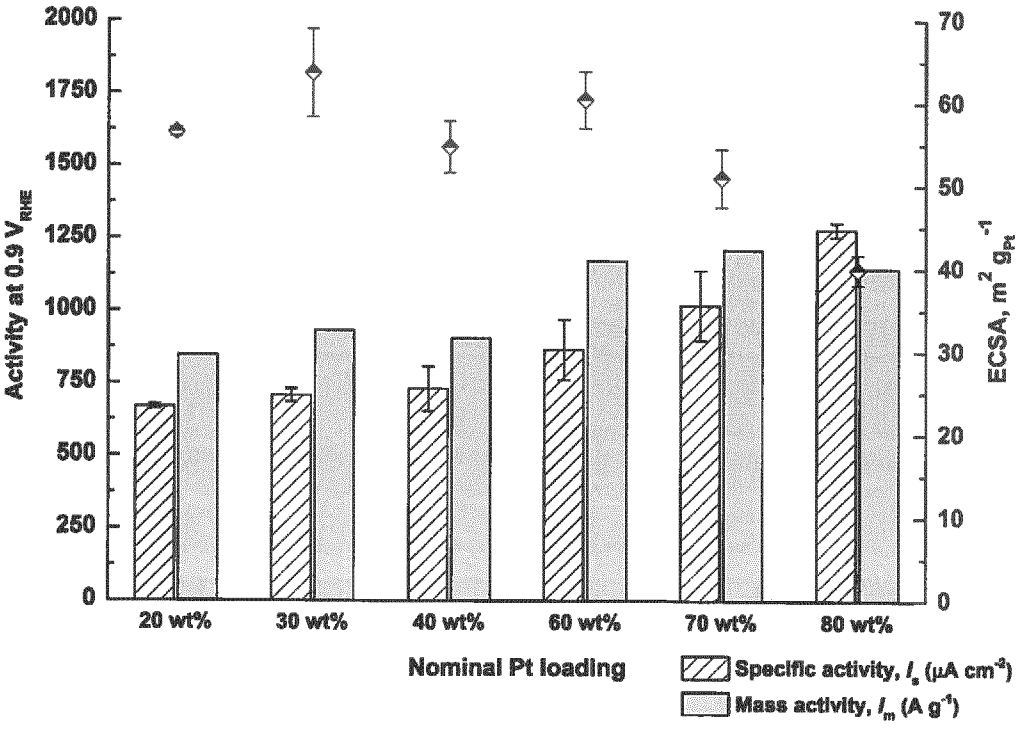

Activity at 0.9 V_{RHE}
ECSA, $m^2 g_{Pt}^{-1}$
2000
1750
1500
1250
1000
750
500
250
0
70
60
50
40
30
20
10
0
20 wt%
30 wt%
40 wt%
60 wt%
70 wt%
80 wt%
Nominal Pt loading
Specific activity, I_s (μA cm^{-2})
Mass activity, I_m (A g^{-1})

Fig. 10

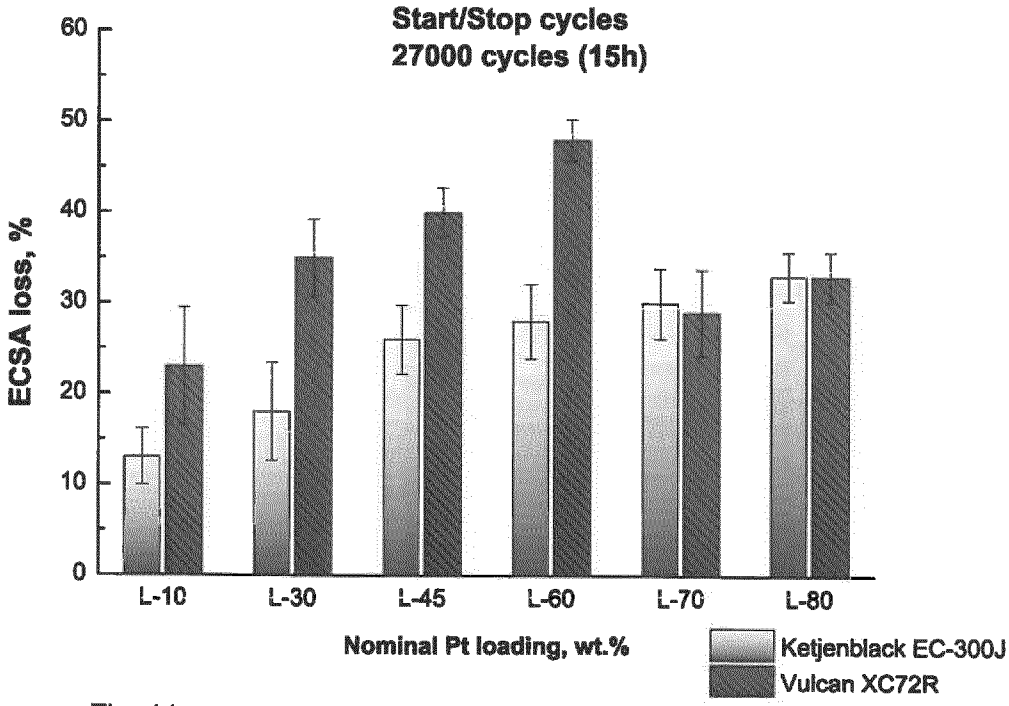

Start/Stop cycles
27000 cycles (15h)
ECSA loss, %
0
10
20
30
40
50
60
L-10
L-30
L-45
L-60
L-70
L-80
Nominal Pt loading, wt.%
Ketjenblack EC-300J
Vulcan XC72R

Fig. 11

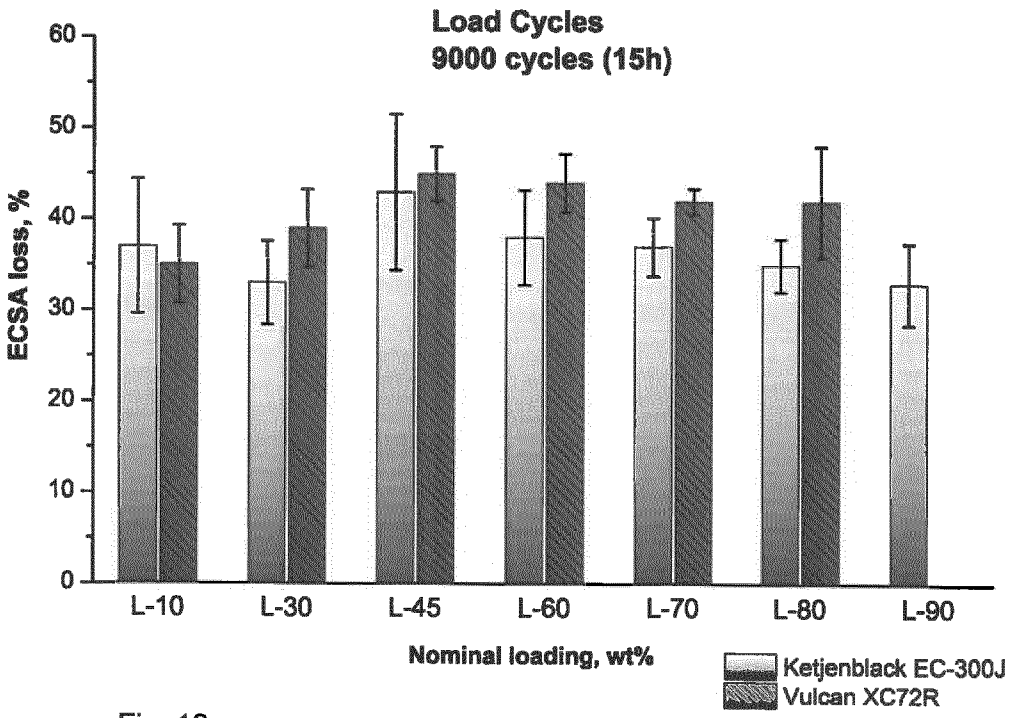

Load Cycles
9000 cycles (15h)
ECSA loss, %
0
10
20
30
40
50
60
L-10
L-30
L-45
L-60
L-70
L-80
L-90
Nominal loading, wt%
Ketjenblack EC-300J
Vulcan XC72R

Fig. 12

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/067874

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J23/42 B01J35/10 B01J35/00 H01M4/00 B01J23/60
B01J23/62 B01J23/648 B01J23/63 B01J23/652 B01J23/89
B01J23/50 B01J23/52 B01J23/46 B01J23/656

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)
B01J 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	CORRADINI P G: "Effect of the relationship between particle size, inter-particle distance, and metal loading of carbon supported fuel cell catalysts on their catalytic activty", JOURNAL OF NANOPARTICLE RESEARCH, KLUWER ACADEMIC PUBLISHERS, DORDRECHT, NL, vol. 14, 4 August 2012 (2012-08-04), page 1080,9pp, XP009163281, ISSN: 1388-0764, DOI: 10.1007/S11051-012-1080-5 abstract page 2, right-hand column, line 10 - page 4, right-hand column, line 2 figures 1,2 table 1 ----- -/--	1-12

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

[X] See patent family annex.

* Special categories of cited documents :

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"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	Date of mailing of the international search report
15 October 2013	06/11/2013

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	Fischbach, Malaika

1

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JALAN V ET AL: "Importance of interatomic spacing in catalytic reduction of oxygen in phosphoric acid", JOURNAL OF THE ELECTROCHEMICAL SOCIETY, ECS, vol. 130, no. 11, 1 January 1983 (1983-01-01), pages 2299-2302, XP009163251, ISSN: 0013-4651, DOI: 10.1149/1.2119574 page 2299, left-hand column, line 47 - page 2300, right-hand column, line 34 figures 1,2	1-12
X	MYOUNG-KI MIN ET AL: "Particle size and alloying effects of Pt-based alloy catalysts for fuel cell applications", ELECTROCHIMICA ACTA, ELSEVIER SCIENCE PUBLISHERS, BARKING, GB, vol. 45, no. 25-26, 1 January 2000 (2000-01-01), pages 4211-4217, XP002671799, ISSN: 0013-4686, DOI: 10.1016/S0013-4686(00)00553-3 abstract page 4216, right-hand column, line 8 - page 4217, left-hand column, line 13 figure 7 table 1	1-12
X	ANTOLINI E: "Physical and morphological characteristics and electrochemical behaviour in PEM fuel cells of PtRu/C catalysts", JOURNAL OF SOLID STATE ELECTROCHEMISTRY, SPRINGER, BERLIN, DE, vol. 5, no. 2, 1 January 2001 (2001-01-01) , pages 131-140, XP009163274, ISSN: 1432-8488 abstract page 136, left-hand column, line 28 - page 136, right-hand column, line 1 table 1 figure 8	1-12
X	EP 1 769 846 A1 (SUMITOMO ELECTRIC INDUSTRIES [JP]) 4 April 2007 (2007-04-04) abstract paragraphs [0002], [0006], [0030] - [0034], [0045], [0066] - [0070] examples 1-16 table 1 claims 1,4,7,8,10,13	1-12

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/067874

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 325 567 A2 (TANAKA PRECIOUS METAL IND [JP]; WATANABE MASAHIRO [JP]; STONEHART PAUL) 26 July 1989 (1989-07-26) cited in the application abstract page 2, lines 38-48 example 1 claims 1-5 figure 3 -----	1-12

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2013/067874

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1769846 A1	04-04-2007	CA 2565113 A1	22-12-2005
		CN 1968746 A	23-05-2007
		EP 1769846 A1	04-04-2007
		KR 20070028523 A	12-03-2007
		US 2007244003 A1	18-10-2007
		US 2010184586 A1	22-07-2010
		WO 2005120703 A1	22-12-2005
EP 0325567 A2	26-07-1989	DE 68911323 D1	27-01-1994
		DE 68911323 T2	07-07-1994
		EP 0325567 A2	26-07-1989
		JP 2977199 B2	10-11-1999
		JP H0265064 A	05-03-1990