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(54) Title: COST-EFFECTIVE CORE-SHELL CATALYST WITH HIGH ELECTROCHEMICAL STABILITY

(57) Abstract: The present invention concerns a core-shell composite material comprising: - a core consisting of Nb-doped TiO₂ of formula TiNbO_x; and - a shell consisting of a homogeneous layer of Pt or Pt alloy of 1 to 50 ML in thickness. The core-shell composite material may in particular find application in fuel cells.



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Cost-effective core-shell catalyst with high electrochemical stability

The present invention relates to a core-shell composite material that may in particular find application in fuel cells, as well as processes that may be used
5 to prepare the core-shell composite material.

Background of the invention

In typical low temperature fuel cells, of considerable interest in the automotive field, hydrogen (H_2), or an organic material with high hydrogen
10 content, supplied to the anode, is oxidized with the release of electrons, whilst at the cathode, oxygen (O_2) is reduced. Platinum (Pt) is a highly active material acting as a catalyst in such fuel cells, and can be used at both the cathode and anode. At the cathode, platinum catalysts are commonly employed to assist in the oxygen reduction reaction (ORR).

15 Conventional fuel cell catalysts are typically based on Pt or Pt-alloy nanoparticles deposited on carbon supports. However, the high cost of these materials and limited electrochemical stability impede their use in commercial fuel cell powered devices. Very fine platinum (Pt) particle dispersions (1 to 2 nm) have been considered to minimize the precious metal loading without
20 losing catalyst activity. However the ORR activity of Pt-catalysts is particle size dependent: the maximum mass activity is obtained with 3 to 4 nm Pt particles. An optimal mass/cost benefit with an ultra-fine Pt dispersion has thus not been achieved. A Pt (or Pt-alloy) particle deposited on a carbon-type support is illustrated in Fig.1. Such a system has a maximum mass activity and specific
25 activity for particles of 3-4 nm, impeding the cost-effective reduction of Pt loading via a finer dispersion (particle diameter < 3 nm). The Pt-based catalyst suffers from dissolution and sintering, while the carbon support is subject to corrosion.

Recently, to reduce the Pt loading by enhancing Pt utilization and
30 activity, some groups have developed core-shell nano-catalysts based on a

precious metal core or a base metal core (such as nickel). With a precious metal core, the resulting material is still expensive, but a base metal core risks being unstable in an electrochemical and acid environment.

Examples of core-shell type catalysts are described in US20100197490, 5 US20070031722, and US20090117257. This type of system is shown schematically in Fig.2, being based on a Pt shell and a noble metal core. This enhances the catalytic activity but does not provide reasonable cost. A core-shell type catalyst, as described in CN101455970 and shown schematically in Fig. 3, based on a Pt shell and a transition metal core, enhances catalytic 10 activity but does not provide reasonable electrochemical stability. The core-shell type catalyst described in US20060263675, and shown schematically in Fig. 4, based on a Pt shell and a bronze WO_3 core, offers a possible solution to the durability issue, but no evidence is provided. With a Pt shell limited to very few atomic layers (<3) the ORR activity could suffer a large overpotential, due to a 15 strong interaction between the oxide substrate and the Pt overlayer.

Summary of the invention

It has now been found that a core-shell composite material comprising an Nb-doped TiO_2 core and a shell consisting of a few atomic layers 20 of Pt, or Pt alloy, can provide a cost-effective alternative to existing Pt-based fuel cell catalysts, whilst providing electrochemical stability and electrical conductivity. The proposed new core-shell catalyst has ORR activities provided by the Pt thin shell that are comparable to that of a polycrystalline Pt thin film and excellent electrochemical stability provided by the oxide core. The core-shell 25 composite materials according to the invention may be prepared in the form of a thin film with a planar underlying Nb-doped TiO_2 layer and a planar overlying Pt or Pt alloy layer. The core-shell composite materials according to the invention may also be prepared in the form of a particle, wherein the core is an Nb-doped TiO_2 nanoparticle having a particle diameter of at least 2 nm

and at most 100 nm, and the shell, deposited on the surface of the Nb-doped TiO₂ nanoparticle core, is a Pt or Pt alloy. The latter, "nanoparticle" aspect of the present invention is schematically illustrated in Figure 6.

In the present invention, an essentially homogeneous layer of Pt or Pt alloy, not consisting of discrete Pt or Pt alloy particles, is laid down on the underlying layer / core of Nb-doped TiO₂.

Thus, the present invention relates to a core-shell composite material comprising :

- a core consisting of Nb-doped TiO₂ of formula TiNbO_x; and
- a shell consisting of a homogeneous layer of Pt or Pt alloy of 1 to 50 ML in thickness.

The unit ML (monolayer) corresponds to a thickness in terms of numbers of atoms. More precisely, in this context, a monolayer (ML) corresponds to the number of equivalent monolayers of platinum (Pt) should the platinum grow in its usual face-centred cubic (FCC) structure, i.e. 1 ML corresponds to one atomic layer of Pt growing in the face-centred cubic structure.

The present invention also relates to a process for the preparation of a core-shell composite material comprising the steps of:

- (1) preparation of a TiNbO_x core, which may be in the form of a thin film or a (nano)particle;
- (2) chemical reduction of the surface of the TiNbO_x core;
- (3) deposit of a homogeneous layer of platinum or platinum alloy on the reduced surface of the TiNbO_x core obtained in step (2).

Brief description of the Figures

Fig.1 shows the conventional catalyst: Pt (or Pt-alloy) particles deposited on a carbon-type support as is commercially available.

Fig. 2 shows a core-shell catalyst based on Pt shell on precious metal core (as known from US2010197490, US2007031722, US2009117257)

Fig. 3 shows a core-shell catalyst based on a Pt shell on a base metal core (as known from CN101455970)

Fig. 4 shows a core-shell catalyst based on a Pt shell and bronze WO_3 oxide core (as known from US20060263675)

5 Fig. 5 shows a Pt-particle catalyst on oxide support as disclosed in embodiments of international application PCT/EP 2010/005907 (filed 28 September 2010)

Fig. 6 shows a schematic representation of a core-shell particle composite material according to the "nanoparticle" aspect of the present
10 invention.

Fig. 7 shows XRD spectra of niobium-doped TiO_x deposited on silicon substrate at 600°C using molecular O_2 at 5.0×10^{-6} Torr.

Fig. 8 shows a Vegard plot demonstrating the rutile lattice expansion of niobium-doped titanium oxide deposited on titanium rotating disk electrode (RDE) substrates at 600°C using 5.0×10^{-6} Torr molecular oxygen.
15

Fig. 9 shows an amorphous TiNbO_x (3.6 to 9.1 at.% Nb) library prepared at 25°C using 5.0×10^{-6} Torr molecular oxygen, after exposure to 0.1 M H_2SO_4 at 80°C for a) 0 hours; b) 2 hours; c) 4 hours; d) 6 hours; e) 24 hours. Each field of the library represents a different Nb composition.

20 Fig. 10 shows a rutile TiNbO_x (3.1 to 12.8 at.% Nb) library prepared at 600°C using 5.0×10^{-6} Torr molecular oxygen, after exposure to 0.1 M H_2SO_4 at 80°C for a) 0 hours; b) 2 hours; c) 4 hours; d) 6 hours; e) 24 hours. Each dot of the library represents a different Nb composition. The atomic percentage stated is on a metal basis, i.e. excluding the oxygen content.

25 Fig. 11 shows the conductivity of as-deposited $\text{Ti}_y\text{Nb}_{(1-y)}\text{O}_x$ films prepared using 5.0×10^{-6} Torr of molecular oxygen on glass substrates at 25°C (amorphous, triangles) and on quartz substrates at 600°C (rutile, diamonds).

Fig. 12 shows a plot of Pt film thickness versus deposition time, including the linear best fit line used for calibration of the films deposited on the oxide substrates.

Fig. 13 shows a second negative going cycle of voltammetry performed at 20 mV s^{-1} in oxygenated 0.5 M HClO_4 solution, but with no electrode rotation, for a range of different equivalent thicknesses of platinum on the non-reduced TiNbO_x sample with 6.4 at% Nb.

Fig. 14 shows a second negative going cycle of voltammetry performed at 20 mV s^{-1} in oxygenated 0.5 M HClO_4 solution, but with no electrode rotation, for 1.1 ML equivalent thickness of platinum on a range of non-reduced TiNbO_x sample with varying niobium content.

Fig. 15 shows the second negative going cycle of voltammetry performed at 20 mV s^{-1} in oxygenated 0.5 M HClO_4 solution, but with no electrode rotation, for a range of different equivalent thicknesses of platinum on rutile TiNbO_x 7 at.% Nb having undergone pre-treatment at 700°C with H_2 .

Fig. 16 shows a second negative going cycle of voltammetry performed at 20 mV s^{-1} in oxygenated 0.5 M HClO_4 solution, but with no electrode rotation, for 2.8 ML of platinum on rutile TiNbO_x with varying niobium content having undergone pre-treatment at 700°C with H_2 .

Fig. 17 shows stability cycling voltammetry for non-reduced rutile TiNbO_x with a Nb concentration of 6.4 at.% with an equivalent thickness of Pt of 11.3 ML, performed at 100 mV s^{-1} in 0.5 M HClO_4 at 25°C.

Fig. 18 shows a second negative going cycle of voltammetry performed at 20 mV s^{-1} in oxygenated 0.5 M HClO_4 solution, but with no electrode rotation, after stability cycling for an equivalent thickness of 2.8 ML of platinum supported on rutile TiNbO_x with varying Nb content for samples pre-treated at 700 °C in H_2 .

Fig. 19 shows a second negative going cycle of voltammetry performed at 20 mV s^{-1} in oxygenated 0.5 M HClO_4 solution, but with no electrode rotation,

for an equivalent thickness of 2.8 ML of platinum supported on rutile TiNbO_x with varying Nb content before and after stability cycling for samples pre-treated at 700 °C in H_2 .

Fig. 20 shows a second negative going cycle of voltammetry performed at 20 mV s^{-1} in oxygenated 0.5 M HClO_4 solution, but with no electrode rotation, after stability cycling for an equivalent thickness of 2.8 ML of platinum supported on TiNbO_x with varying Nb content for samples pre-treated at 700 °C in H_2 .

Fig. 21 shows a second negative going cycle of voltammetry performed at 20 mV s^{-1} in oxygenated 0.5 M HClO_4 solution at 25°C, but with no electrode rotation for a range of different Pt/ TiNbO_x samples.

Fig. 22 shows the mass specific current density versus core diameter for various Pt shell thicknesses, assuming a current density of 7.5 $\mu\text{A}/\text{cm}^2$. The maximum value obtained for 3-4 nm particles of Pt on carbon is shown with the horizontal line.

Detailed description of the invention

The present invention relates to a core-shell composite material comprising :

- a core consisting of Nb-doped TiO_2 of formula TiNbO_x ; and
- a shell consisting of a homogeneous layer of Pt or Pt alloy of 1 to 50 ML in thickness.

In a preferred process for preparing a core-shell particle composite material according to the present invention, the following steps are carried out, step (2) being a preferred intermediate stage between the preparation of the TiNbO_x core and the deposition of the Pt / Pt alloy shell:

- (1) Preparation of the TiNbO_x core, which may be in the form of a thin film or a (nano)particle;
- (2) Chemical reduction of the surface of the TiNbO_x core;

(3) Deposition of a homogeneous layer of platinum or platinum alloy.

Generally applicable and/or advantageous embodiments both with respect to the composition of the core and shell layers, as well as processes for preparing them, will be presented hereinunder. It is to be understood that the present application encompasses any combination of generally applicable and/or advantageous embodiments described in what follows.

In both the "thin film" and "nanoparticle" aspects of the present invention, it is preferred to have at most 25 at. % Nb in the TiNbO_x core/layer. It is to be noted that herein this atomic percentage is defined on a metallic basis, i.e. excluding oxygen, and therefore the atomic percentage of niobium (at. % Nb) gives a relative number of niobium (Nb) atoms compared to the total number of Nb + Ti atoms in the TiNbO_x core/layer. Preferably the amount of Nb is at least 1 at% and at most 15 at% on a metal basis, excluding the oxygen content.

Also, in both the "thin film" and "nanoparticle" aspects of the present invention, it is preferred for the TiNbO_x to be in the rutile phase. In effect, it is believed that amorphous TiNbO_x is likely to provide materials with instability with respect to the acid environment. It is therefore preferred to have a TiNbO_x core/layer as highly crystalline as possible, in the rutile phase.

As regards thin film embodiments of the present invention, a composite oxide layer comprising Nb-doped TiO_2 can be synthesized by different methods, for instance PVD methods (i.e. molecular beam deposition, vacuum deposition, ion plating or sputtering) on different types of substrates, such as Si, glass, Si/TiW, etc. Preferably physical vapour deposition from metal sources (titanium and niobium metal) in molecular or oxygen plasma is carried out.

When deposition is carried out, it is preferable to supply oxygen gas at a pressure of 1×10^{-7} to 5×10^{-5} Torr, and where a plasma is used, with a plasma source power of 300 to 600 W.

Amorphous thin film oxides can be synthesized by depositing the metals whilst using the atomic oxygen plasma source or molecular oxygen without applying any heating to the substrate.

Rutile crystalline composite oxides in film form can be synthesized by heating the substrate at 600 to 800°C. Different oxygen stoichiometries are achievable by depositing the metals using molecular oxygen, or an atomic oxygen plasma source at a power of 400 W, and at a pressure of 5×10^{-7} Torr to 5×10^{-6} Torr of oxygen.

In "thin film" embodiments of the present invention, a generally advantageous thickness of the TiNbO_x layer is at least 5 nm and at most 1000 nm, preferably at least 5 nm and at most 200 nm, and more preferably at least 5 nm and at most 100 nm.

As regards nanoparticle embodiments of the present invention, oxide core nanoparticles can be synthesized by various means known in the art, including solid-state and sol gel, but not limited to those. Suitable solid-state methods for synthesizing metal oxide particles typically include the application of a heating source. For example, particles of TiNbO_x can be produced by heating a combination of the corresponding metal precursors at temperature higher than 1000 °C.

Suitable sol gel methods for synthesizing Nb-doped TiO_2 powders typically include the hydrolytic reaction between metal alkoxides, metal amides, or metal carboxylates. Hydrolysis of the one or more oxide precursors is generally affected by water and can be further aided by catalytic amounts of an acid or base. For example, Nb-doped TiO_2 powders can be prepared by the sol-gel method from the hydrolysis of Ti-isopropoxides and niobium (V) ethoxide. Rutile oxide nanoparticles are obtained after calcination at a temperature of 600 to 1000°C in an oven under an oxygen atmosphere. Sub-stoichiometric compositions can be obtained in a H_2 reducing atmosphere.

Additionally, non-aqueous methods may be advantageous for the synthesis of these core-shell structures. These methods allow better control of a reduced and un-hydroxylated surface to facilitate the formation of the Pt shell. These methods include:

- 5 a) Direct physical vapour deposition (PVD) of the platinum shell onto the Nb-doped TiO₂ core;
- b) Electroless Pt deposition in non-aqueous reducing electrolytic environments directly onto nanoparticle suspensions of the Nb-doped TiO₂ core;
- c) Chemical Fluid Deposition (for example using supercritical CO₂)
- 10 directly onto nanoparticle suspensions of the Nb-doped TiO₂ core.

Concerning the "thin film" and "nanoparticle" aspects of the present invention, it is considered that thin films with an underlying TiNbO_x layer and an overlying (homogeneous) Pt (or Pt alloy) layer show electrocatalytic behavior of the same type as that which will be observed for core-shell systems in which a

15 (homogeneous) Pt (or Pt alloy) shell is laid down on a TiNbO_x (nano)particle core. The thin films may thus be considered a model system which the present inventors consider accurately reflects the properties of (nano)particulate core-shell catalysts with the same chemical nature.

Assuming that the current density obtained on the thin film is at least as

20 high as the maximum specific current density obtained with Pt particles, it is possible to calculate a theoretical value for the mass specific current density, for varying thicknesses of Pt shell on varying core diameters. Such calculations lead to the conclusion that if the film of Pt is less than approximately 5 ML in thickness then an improvement in the mass specific current density should be

25 observed over that seen for the optimal catalyst (3 to 4 nm particles) of carbon-supported Pt particles. Furthermore, in the case that the core diameter can be markedly reduced, it is expected that this would provide additional enhancement in mass specific current density. Figure 22 illustrates this trend.

Consequently, in the (nano)particle aspect of the present invention, it is preferred for the TiNbO_x (nano)particle core to have a particle diameter of at least 2 nm and at most 500 nm, preferably at least 2 nm and at most 100 nm, and most preferably at least 2 nm and at most 50 nm. Concerning the measurement of particle diameters, there are many conventional ways to measure particle diameters lower than 500 nm. For instance this can be measured by diffraction techniques (X-ray Diffraction, Low Angle Laser Light Scattering), electron microscopy techniques (TEM/SEM), adsorption techniques (BET). In the present invention, where methods may give somewhat different results, particle size shall be as observed by X-ray Diffraction (XRD).

In a preferred process step, labelled step (2) above, chemical reduction of the oxide surface is carried out. The aim here is to chemically reduce the surface of the Nb-doped TiO_2 oxide core/layer for particle/thin film embodiments, without significant reduction of the underlying bulk of the oxide core/layer. Reduction of the bulk of the Nb-doped TiO_2 oxide core/layer may lead to electrochemical instability. XPS analysis was used to verify the reduction of the surface whilst X-ray diffraction and ellipsometry were used to confirm that no significant reduction of the bulk has occurred.

The purpose of this reductive pre-treatment is to increase the wetting of the Pt on the surface, and enable a uniform Pt film deposition. The reduction of the oxide surface provides more nucleation sites for Pt, which will be deposited in subsequent step (3). By this means, the surface is covered at the lowest possible "critical thickness" of Pt. The "critical thickness" or "critical film thickness" of Pt herein is the film thickness above which no further reduction in the overpotential of the oxygen reduction reaction (ORR) occurs.

Generally, any surface pre-treatment can be applied that can reduce the surface of the (Nb-doped Ti) oxide without affecting bulk properties. Among specific methods which may advantageously applied may be mentioned:

- Annealing in ultra high vacuum (pressure lower than 10^{-9} Torr) at high temperature (600 to 1000°C) for a short time (5 min to 1 hour) depending on the selected temperature. Preferably the temperature is between 750 and 850°C for a duration of from 20 to 40 min. Currently preferred conditions include treatment at a temperature of about or exactly 800°C for a duration of about or exactly 30 min.
- Annealing in high vacuum (10^{-5} to 10^{-7} Torr) H_2 at 600 to 1000°C for a short time (5 min to 1 hour) depending on the selected temperature and pressure. Preferable conditions are a pressure range of 10^{-6} to 10^{-5} Torr H_2 at 650 to 750°C for 20 to 40 min. Currently preferred conditions include treatment at a (hydrogen) pressure of about or exactly 5×10^{-6} Torr H_2 at a temperature of about or exactly 700°C for a duration of about or exactly 30 min.

On rutile $TiNbO_x$ a polycrystalline-Pt thin film behaviour (equivalent, in terms of overpotential for the oxygen reduction reaction (ORR) to bulk or thin film Pt) is achieved by a critical film thickness of about 5.7 equivalent atomic layers in the illustrative experimental examples. By developing a surface reducing treatment on the rutile $TiNbO_x$, the Pt-like behaviour could be achieved by a lower critical thickness, namely 2.8 equivalent atomic layers in the illustrative experimental examples. The mechanism is not fully clear, but it is believed that the surface reduction treatment enhances Pt wetting on the $TiNbO_x$ substrate.

As for step (3) of the overall preparation process described above, i.e. the deposition of platinum or platinum alloy, various methods can be envisaged for depositing layers of Pt or Pt alloy on the oxide cores, among them Atomic Layer Deposition, Chemical Vapor Deposition and Physical Vapor Deposition. In a currently preferred embodiment, deposition from an electron beam source, or "electron gun", may be used, for a duration of 2 to 30 min. The aim of this stage is to prepare a homogenous, as far as possible uniformly deposited Pt (or

Pt alloy) layer with a thickness of at least 1 ML (monolayer) and at most 50 ML, preferably at least 2 ML and at most 20 ML, more preferably at least 2 ML and at most 10 ML. In a particularly advantageous embodiment, the preferred Pt (or Pt alloy) layer has a thickness of at least 2 ML and at most 5 ML. The number of equivalent monolayers of deposited Pt is calculated from the deposition rate, which is in turn obtained by depositing thicker calibration films. The thickness of these calibration films is measured directly using optical profilometry or atomic force microscopy. The ultra-thin films can be directly observed by Transmission Electron Microscopy which shows the transition from particles to continuous thin films.

Apart from pure platinum (Pt), a Pt alloy may be used in the framework of the present invention. Such a Pt alloy could be a binary, ternary or quaternary alloy comprising noble metals other than platinum and/or transition metals. Examples of a noble metal other than Pt include ruthenium, osmium, rhodium, iridium, palladium, gold and silver. Examples of transition metals include molybdenum, cobalt, iron, nickel, titanium, tungsten, rhenium, chromium, manganese, niobium and tantalum. In a preferred embodiment, a catalyst layer containing Pt only is used.

In the core-shell composite material according to the present invention, it appears that the Nb dopant provides improved electrical conductivity to the oxide, whilst the rutile structure guarantees its electrochemical stability. The pre-treatment process for oxide reduction at the surface of the oxide provides stability to Pt film on cycling when doped with Nb (the pure rutile TiO_x is less stable).

The core-shell composite material according to the present invention may be used in fuel cells, and more generally any low temperature fuel cell where the cathode process is the reduction of oxygen, including polymer electrolyte membrane fuel cells (PEMFC), and other alcohol fuel cells such as

direct methanol fuel cells (DMFC). The core-shell composite material according to the present invention may thus be incorporated into an oxygen-reducing cathode comprising an electrically conductive support upon which is supported a core-shell composite material according to the present invention.

5

Examples

1) Preparation and screening of the core material: thin film Ti-Nb oxide library

10 *Synthesis*

A library of thin film Ti-Nb oxide samples in the amorphous and rutile phases were synthesized with a metal dopant concentration of 0-25 at.% Nb and analyzed for their composition, crystallinity, conductivity and stability in acid. Amorphous TiNbO_x thin films were prepared at 25 °C in 5.0×10^{-6} Torr of molecular oxygen by PVD, whilst rutile films were prepared at 600°C in 5.0×10^{-6} Torr of molecular oxygen across the entire compositional range.

Some of the rutile libraries were submitted to an optimized pre-treatment, to reduce the surface area, prior to Pt deposition.

20 *Crystallinity*

The rutile phase pattern of titanium oxide was observed by XRD with a preferential orientation along the (110) crystal plane. No Nb metal, Nb oxide or TiNbO_x secondary phases were identified, suggesting that the materials consisted of a homogeneous solid solution of Nb in the octahedral sites occupied by the titanium atoms in the TiO₂ rutile crystal structure. The XRD data for the samples synthesized is shown in Figure 7. A linear expansion of the lattice in the [110] direction is observed with increasing Nb concentration which is consistent with Nb substitution for Ti in the rutile, the correlation is reported in Figure 8.

Stability in acid

All rutile films demonstrated resistance to 0.1 M H₂SO₄ at 80 °C over a 24 hour period (Fig. 10) whilst all amorphous (Fig. 9) films were seen to be unstable, dissolving fully over the same time period. ICP-MS measurements performed prior to and after the acid exposure showed a relative slight loss of Nb relative to Ti at higher Nb doping levels, which was attributed to the removal of Nb from interstitial sites at greater than ~15 at. % Nb.

Stability tests have been carried out on the rutile TiNbO_x films which have been pre-treated under the same two sets of conditions mentioned above. No visible change was observed for any of the rutile samples which had been annealed at 800°C in vacuum, or at 700°C in 5.0 x 10⁻⁶ Torr of hydrogen, on exposure to the hot acid.

Conductivity

For each of the relevant thin film oxides prepared on the glass substrates, four point probe (4PP) conductivity measurements were performed in order to obtain their resistivity.

The amorphous and rutile films both had a conductivity of ~ 0.03 S cm⁻¹ for 0 at.% Nb (Fig. 11). Increasing the concentration of the Nb dopant leads to an increased conductivity for the rutile films up to 10 S cm⁻¹ at 33 at.%, whilst the addition of Nb has little effect on the conductivity of the amorphous materials.

2) Preparation and characterization of the ultrathin Pt film on the oxide libraries

Synthesis

Platinum thin films were deposited from an electron gun source onto the relevant oxide-covered samples for electrochemical screening.

For all samples the deposition times varied from 1 to 30 minutes, which produced films with a thickness corresponding to approximately 0.6 to 17 equivalent monolayers (Fig. 12). The films were deposited at 200°C to dehydroxylate the surface of the doped titania supports and lead to the formation of a stable Pt film.

Characterization of the Pt deposited films

These systems were then investigated for activity towards the ORR and stability on potential cycling in 0.5 M HClO₄. Electrochemical screening of the rutile TiNbO_x-supported Pt thin films demonstrated (Fig. 13) that the overpotential required for the oxygen reduction reaction (ORR) remained fairly constant at the higher equivalent thicknesses, but at the lowest equivalent thickness was significantly increased. Pt-polycrystalline behavior is achieved by a film thickness of 5.7 equivalent atomic layers. Above this value little change is observed. For sake of comparison, ultrathin films of Pt on amorphous TiNbO_x required a higher critical film thickness of 8 equivalent atomic layers to achieve a Pt-polycrystalline behavior.

It could be observed (Fig. 14) that for very low Pt thickness (1.1 equivalent atomic layer) on rutile oxides the onset potential for oxygen reduction is not significantly different on all of the rutile supports containing niobium, but that the onset for oxygen reduction on rutile titania without any niobium has been shifted to a much lower potential (i.e. the overpotential has increased). This would suggest that the addition of Nb has a positive effect. Moreover, after the addition of a few percent of Nb, no significant further enhancement in activity can be obtained from further addition of Nb above approximately 10 at.%.

On surface reduced rutile TiNbO_x (Fig. 15) there is not a significant difference in the overpotential for oxygen reduction as the equivalent thickness of platinum is decreased to 2.8 ML (however the lower coverages tend to have the highest overpotentials). Below 2.8 ML equivalent thickness a significant increase in overpotential for the oxygen reduction reaction is seen.

Fig. 16 shows the oxygen reduction data for a Pt equivalent thickness of 2.8 ML on all of the different rutile TiNbO_x supports which underwent a pre-treatment of 700 °C in H_2 . All of the electrodes have a very similar overpotential for the oxygen reduction reaction. The electrode with 4.1 at. % Nb has a slightly lower overpotential, suggesting it is slightly more active.

Electrochemical stability

200 cycles from 0.025 – 1.200 V at 100 mV s⁻¹ were performed in deoxygenated 0.5 M HClO_4 on the samples that had previously undergone the O_2 reduction experiment procedure outlined above. On most of the non-reduced rutile samples (Fig. 17) after 30 stability cycles the cyclic voltammetry appeared to remain constant. In Fig. 17 for example it can be seen that the 30th, 100th and 200th CV cycles for the sample TiNbO_x with 11.4 at.% Nb and 11.3 ML Pt are very similar, suggesting that the platinum and support are fairly stable.

Indeed, the charges associated with hydrogen adsorption/desorption and Pt oxide formation/reduction increase during the first 30 cycles and then stabilise. This could be due to a slight roughening of the surface, or even electrochemical cleaning of the electrode surface.

Stability cycling has demonstrated that the non-reduced rutile films (Fig. 18) with a coverage of < 2.8 ML have a high overpotential for the onset of surface oxide reduction (which is intrinsically related to the oxygen reduction potential). There is evidence of sintering of the films of 4.0 and 5.7 ML thickness to form particles, whilst those of 8.5 ML and above demonstrate

polycrystalline Pt-like behavior. These are stable on cycling, but show evidence of surface roughening. No significant effect due to the Nb content of the support films was observed.

The oxygen reduction data before and after stability cycling for 2.8 ML equivalent thickness of Pt on the full range of supports is shown in Figure 19. Above 4.1 at.% Nb the overpotential for oxygen reduction does not change (or is shifted to lower overpotential). For both the support with no niobium doping and the support containing 4.1 at.% doping, the overpotential for the oxygen reduction reaction appears to increase after stability cycling. This suggests that with a low level of niobium doping, the electrodes pre-treated to 700 °C in H₂ are not so stable towards oxygen reduction activity.

Figure 20 shows a comparison of the oxygen reduction data after stability cycling for 2.8 ML equivalent thickness of Pt on all of the different reduced rutile TiNbO_x supports. All of the supports containing niobium have a similar overpotential for the reaction after stability cycling (although the support with 4.1 % Nb has shifted to the highest overpotential of the supports containing Nb). The electrode containing no niobium doping has the highest overpotential for the reaction after stability cycling, suggesting it is the least active after stability cycling has taken place.

Effect of pre-treatment on the ORR activity

Finally, Figure 21 summarizes the oxygen reduction data for a range of different oxide/Pt combinations. This shows the reduction in the overpotential observed, initially from the addition of small amounts of Nb to the support, then due to the crystallization of the support into the anatase and rutile phases, a further enhancement due to the use of the core shell model, and finally due to the preparation of the core shell model catalysts with the surface of the oxide support reduced (using the pre-treatment of the sample under the two selected sets of conditions).

Claims

1. A core-shell composite material comprising :
 - a core consisting of Nb-doped TiO_2 of formula TiNbO_x ; and
 - 5 - a shell consisting of a homogeneous layer of Pt or Pt alloy of 1 to 50 ML in thickness.
2. A core-shell composite material according to claim 1, wherein the TiNbO_x core, prior to laying down of the Pt or Pt alloy shell, has been subjected to a
10 process to reduce the surface of the TiNbO_x core.
3. A core-shell composite material according to claim 2, wherein the process to reduce the surface of the TiNbO_x core comprises annealing in ultra high vacuum, at a pressure lower than 10^{-9} Torr, at a temperature of 600 to
15 1000°C , for a duration of 5 minutes to 1 hour.
4. A core-shell composite material according to claim 2, wherein the process to reduce the surface of the TiNbO_x core comprises in treatment in a hydrogen atmosphere of 10^{-5} to 10^{-7} Torr H_2 , at a temperature of 600 to
20 1000°C , for a duration of 5 minutes to 1 hour.
5. A core-shell composite material according to any of claims 1 to 4, wherein the amount of Nb in the TiNbO_x core is at most 25 at% on a metal basis, excluding the oxygen content.
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6. A core-shell composite material according to claim 5, wherein the amount of Nb in the TiNbO_x core is at least 1 at% and at most 15 at% on a metal basis, excluding the oxygen content.

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7. A core-shell composite material according to any of claims 1 to 6, wherein the TiNbO_x is in the rutile phase.

8. A core-shell composite material according to any of claims 1 to 7,
5 wherein the thickness of the Pt or Pt alloy shell is of at least 2 ML and at most 20 ML.

9. A core-shell composite material according to claim 8, wherein the thickness of the Pt or Pt alloy shell is of at least 2 ML and at most 5 ML.

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10. A core-shell composite material according to any of claims 1 to 9, wherein the material is in the form of a thin film with a planar underlying Nb-doped TiO_2 layer and a planar overlying Pt or Pt alloy layer.

11. A core-shell composite material in the form of a thin film according to claim 10, wherein the TiNbO_x core layer thickness is at least 5 nm and at most 1000 nm.

12. A core-shell composite material in the form of a thin film according to claim 11, wherein the TiNbO_x core layer thickness is at least 5 nm and at most 200 nm.

13. A core-shell composite material in the form of a thin film according to claim 11, wherein the TiNbO_x core layer thickness is at least 5 nm and at most 100 nm.

14. A core-shell composite material according to any of claims 1 to 9, wherein the material is in the form of a particle, wherein the core is an Nb-doped TiO_2 nanoparticle having a particle diameter of at least 2 nm and at most

500 nm, and the shell, deposited on the surface of the Nb-doped TiO₂ nanoparticle core, is a Pt or Pt alloy.

15. A core-shell composite material according to claim 14, wherein the core
5 is an Nb-doped TiO₂ nanoparticle having a particle diameter of at least 2 nm and at most at most 100 nm.

16. A core-shell composite material according to claim 15, wherein the core
10 is an Nb-doped TiO₂ nanoparticle having a particle diameter of at least 2 nm and at most at most 50 nm.

17. Process for the preparation of a core-shell composite material comprising the steps of:

(1) preparation of a TiNbO_x core, which may be in the form of a thin film
15 or a (nano)particle;

(2) chemical reduction of the surface of the TiNbO_x core;

(3) deposit of a homogeneous layer of platinum or platinum alloy on the reduced surface of the TiNbO_x core obtained in step (2).

18. Process according to claim 17, wherein the process to reduce the surface of the TiNbO_x core comprises annealing in ultra high vacuum, at a pressure lower than 10⁻⁹ Torr, at a temperature of 600 to 1000°C, for a duration of 5 minutes to 1 hour.

19. Process according to claim 17, wherein the process to reduce the surface of the TiNbO_x core comprises in treatment in a hydrogen atmosphere of 10⁻⁵ to 10⁻⁷ Torr H₂, at a temperature of 600 to 1000°C, for a duration of 5 minutes to 1 hour.

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20. Process according to any of claims 17 to 19, wherein the TiNbO_x core is prepared in the rutile phase.

21. Process according to any of claims 17 to 20, wherein the amount of Nb
5 in the TiNbO_x core is at most 25 at% on a metal basis, excluding the oxygen content.

22. Process according to any of claims 17 to 21, wherein the thickness of the Pt or Pt alloy shell is of at least 2 ML and at most 20 ML.

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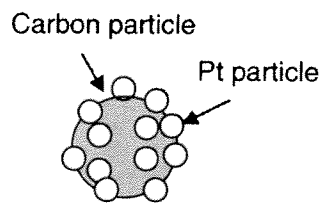


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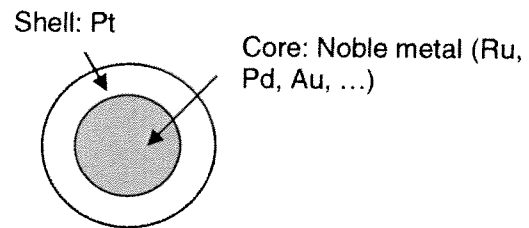


Fig. 2

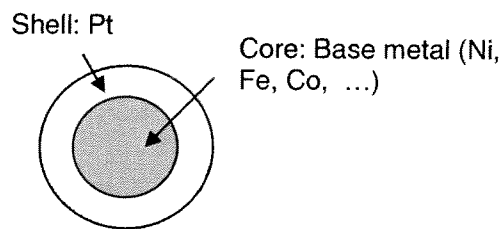


Fig. 3

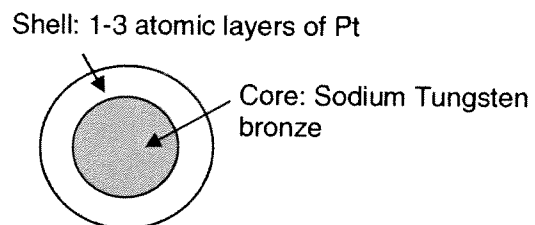


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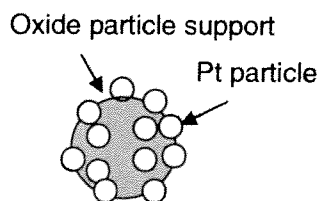


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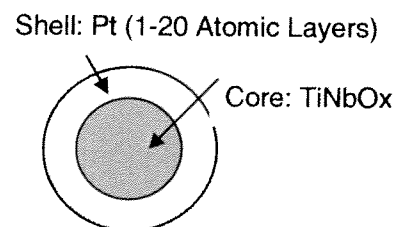


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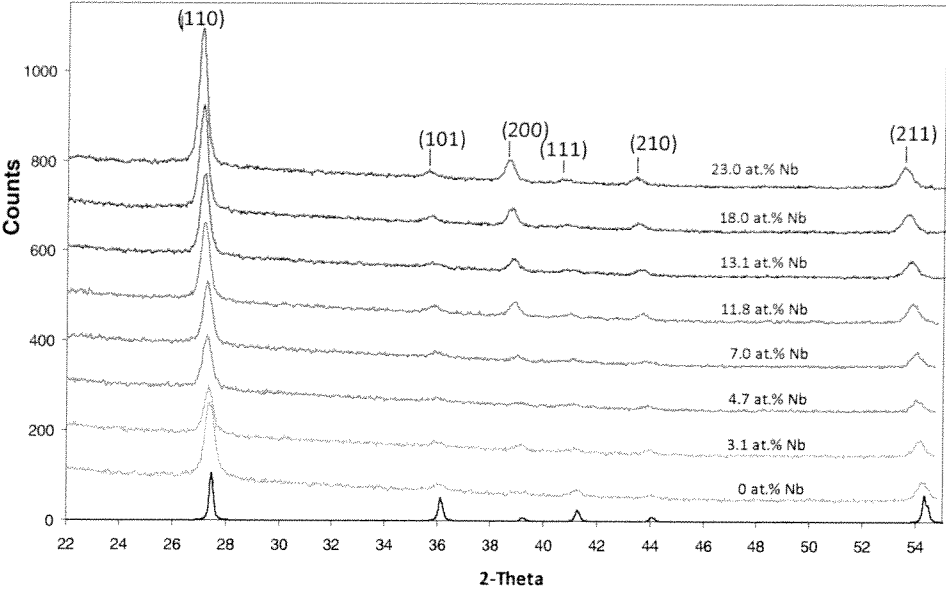


Fig. 7

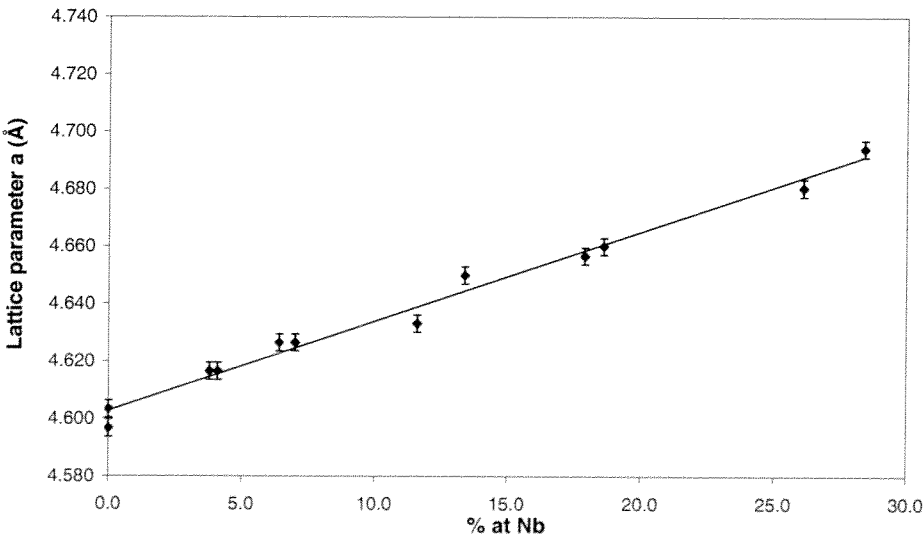


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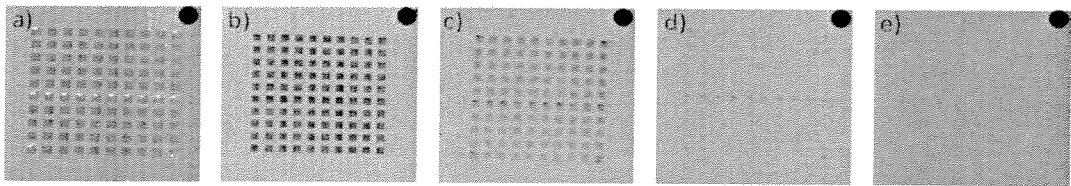


Fig. 9

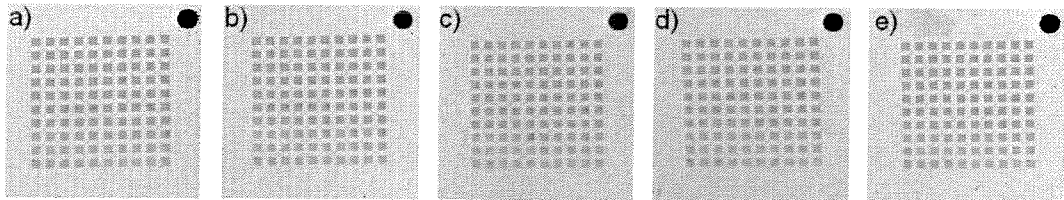


Fig. 10

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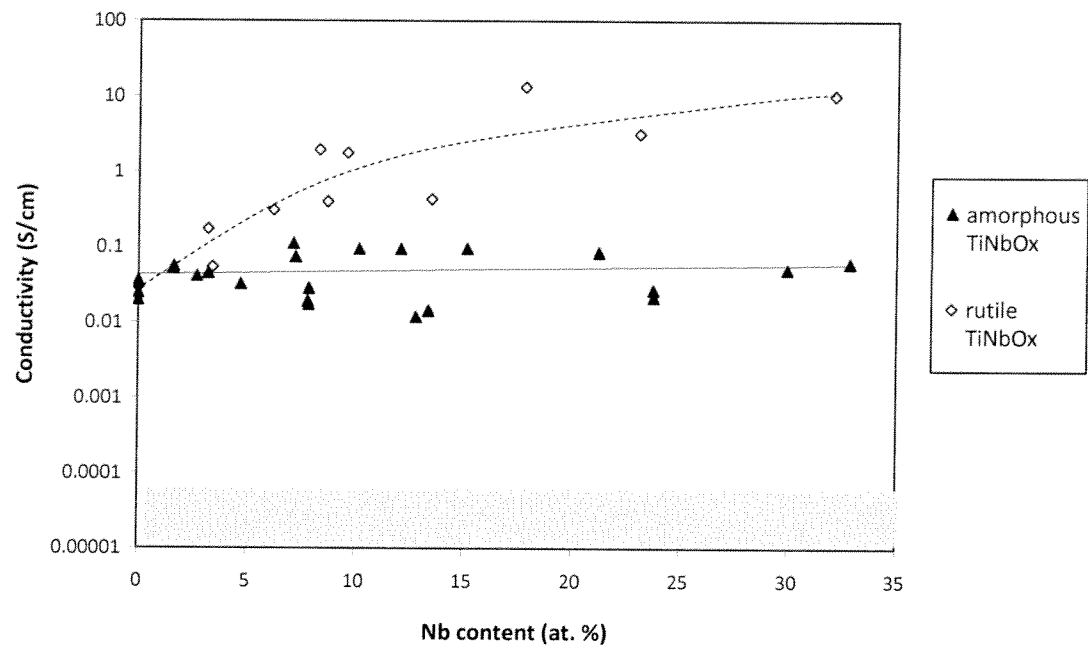


Fig. 11

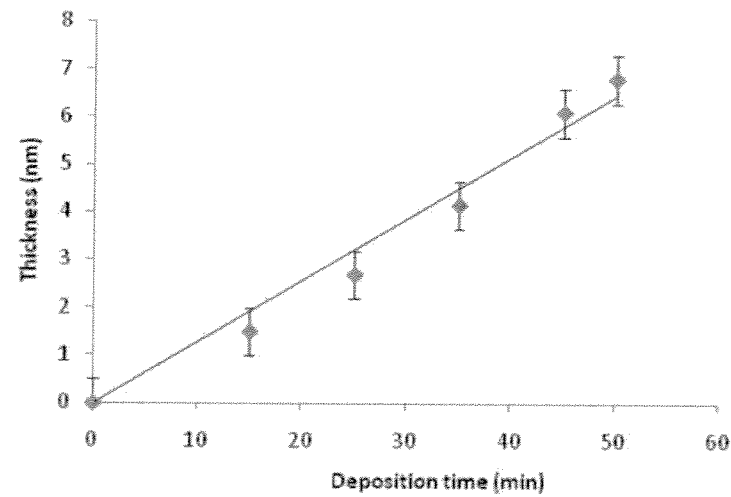


Fig. 12

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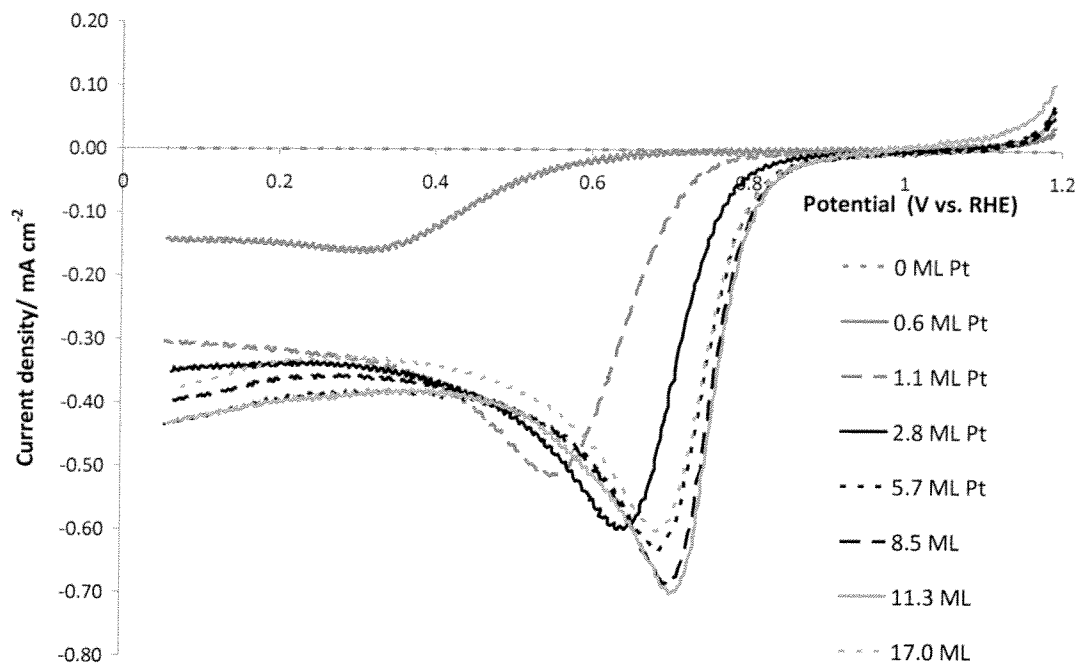


Fig. 13

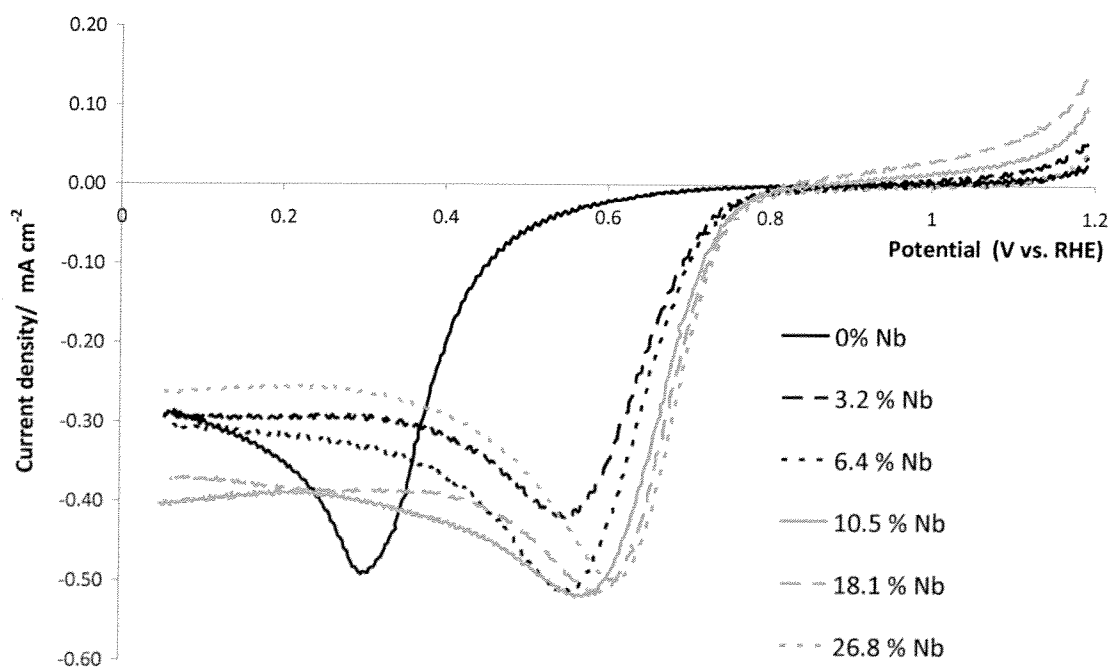


Fig. 14

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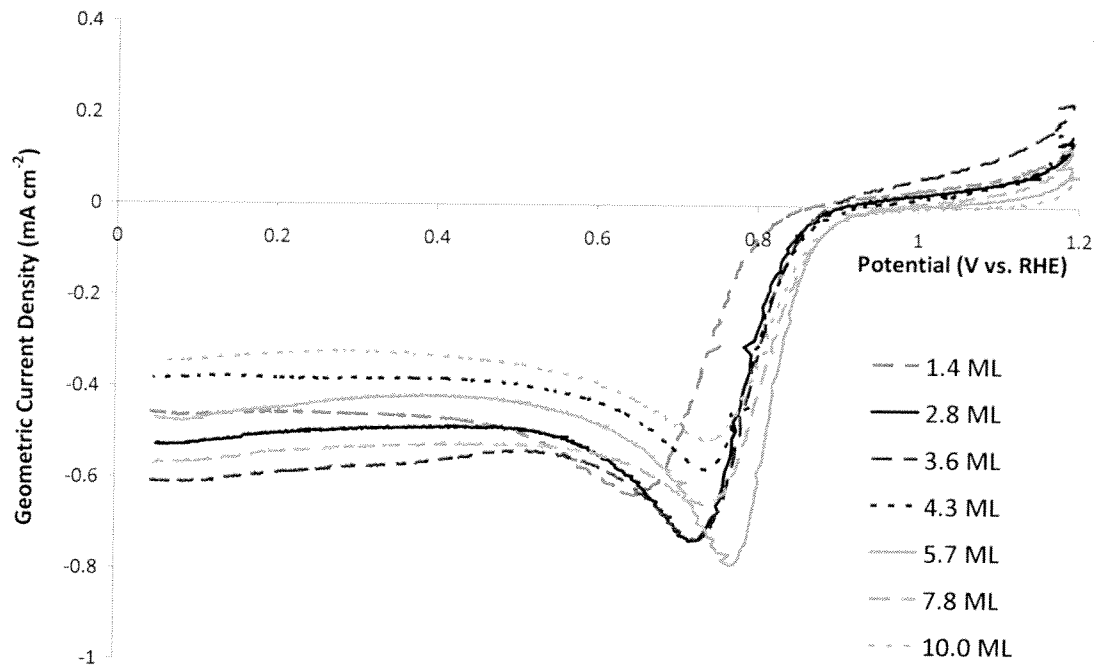


Fig. 15

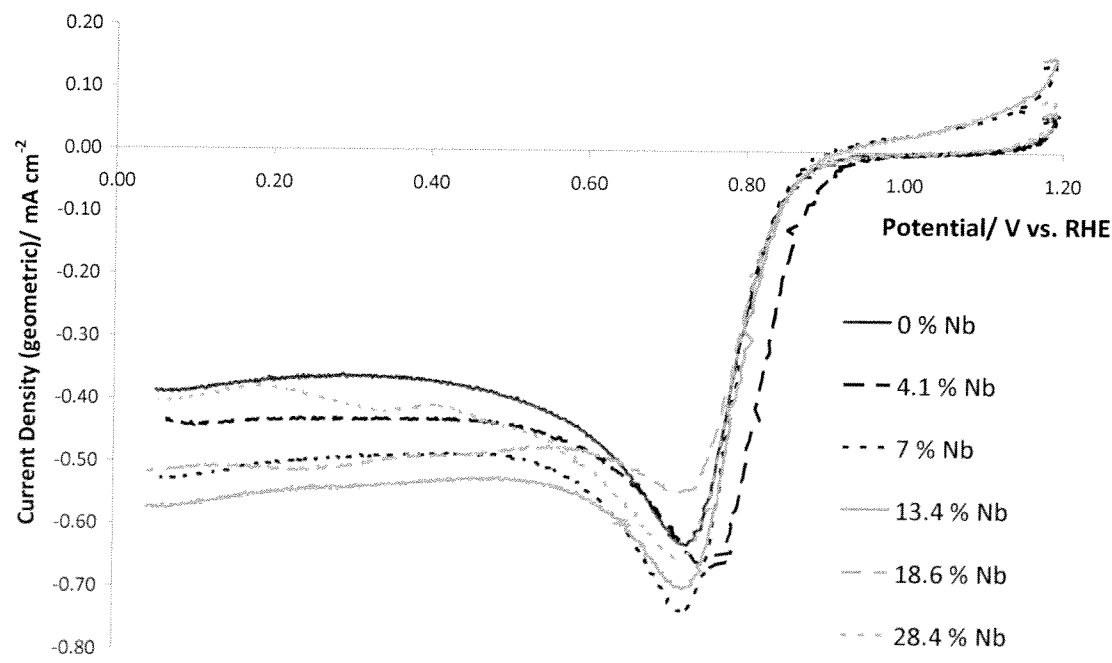


Fig. 16

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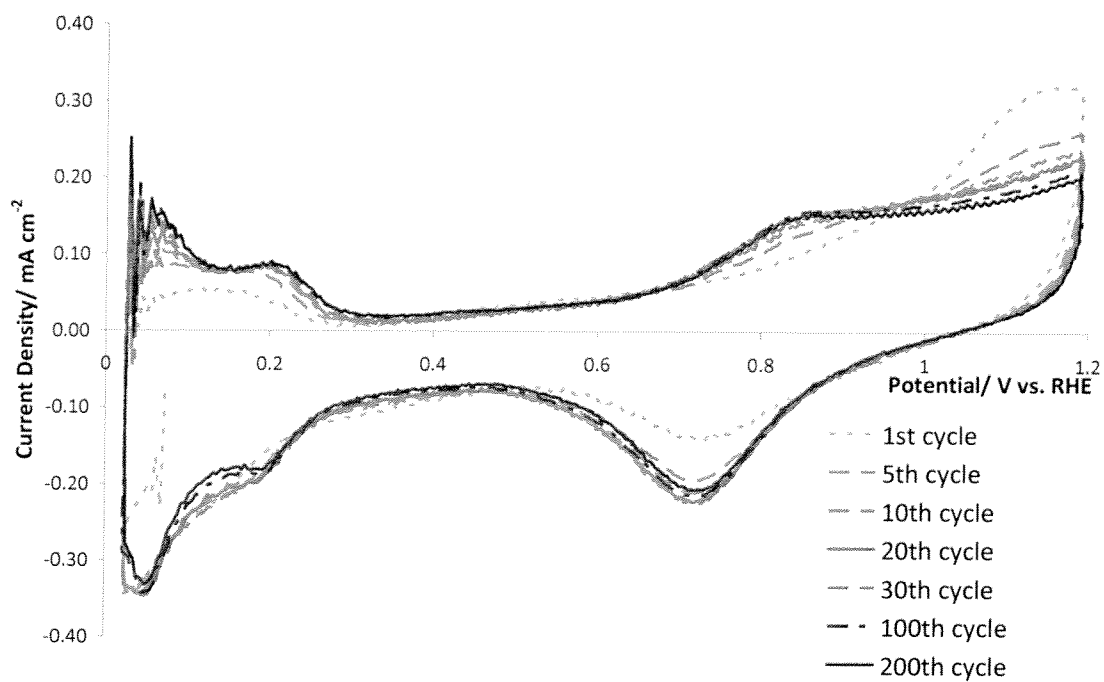


Fig.17

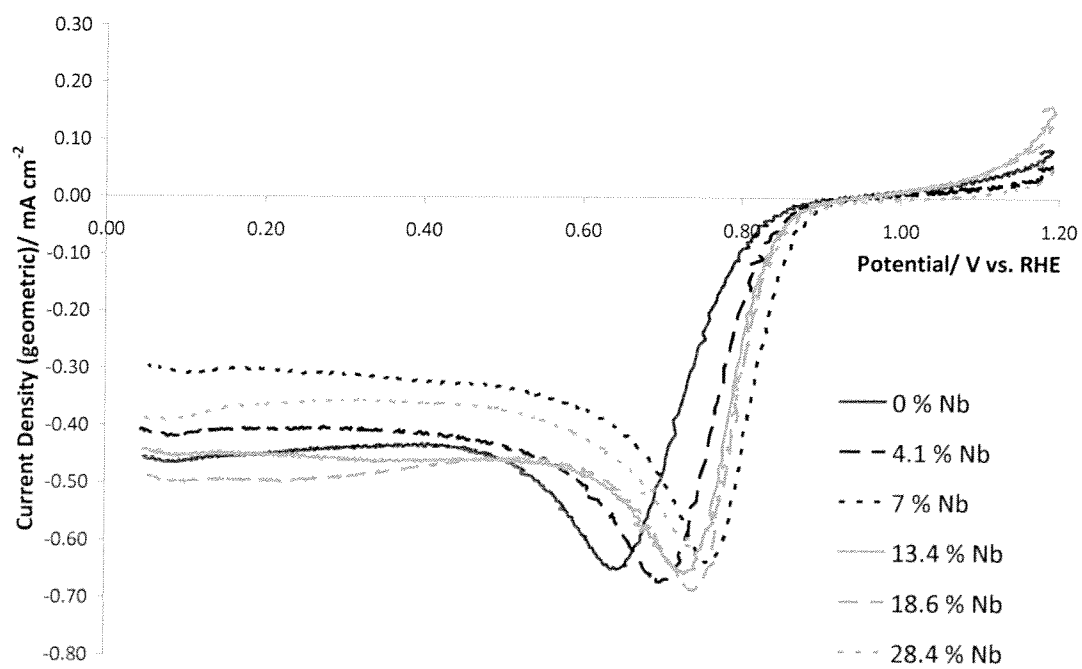


Fig.18

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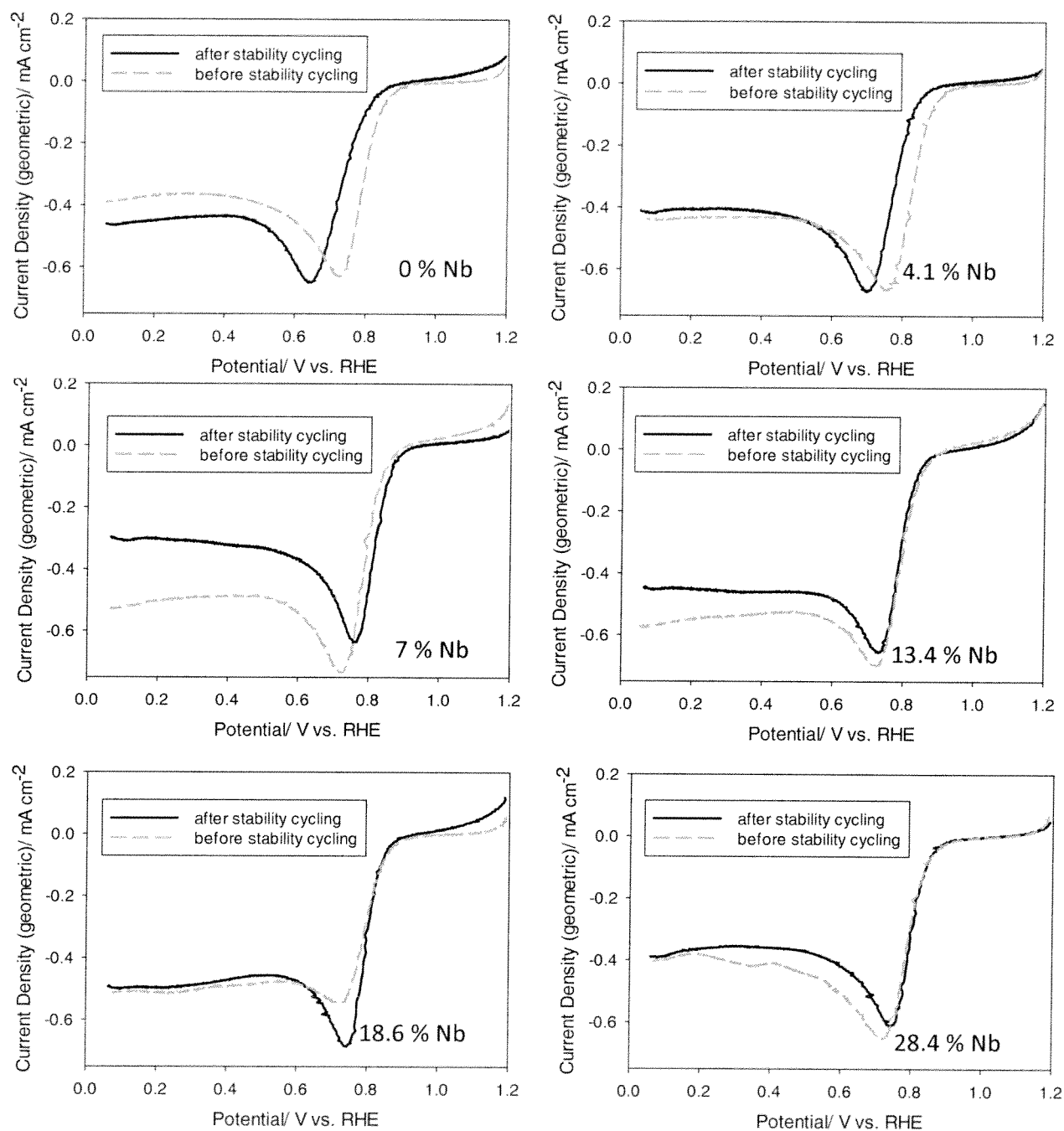


Fig. 19

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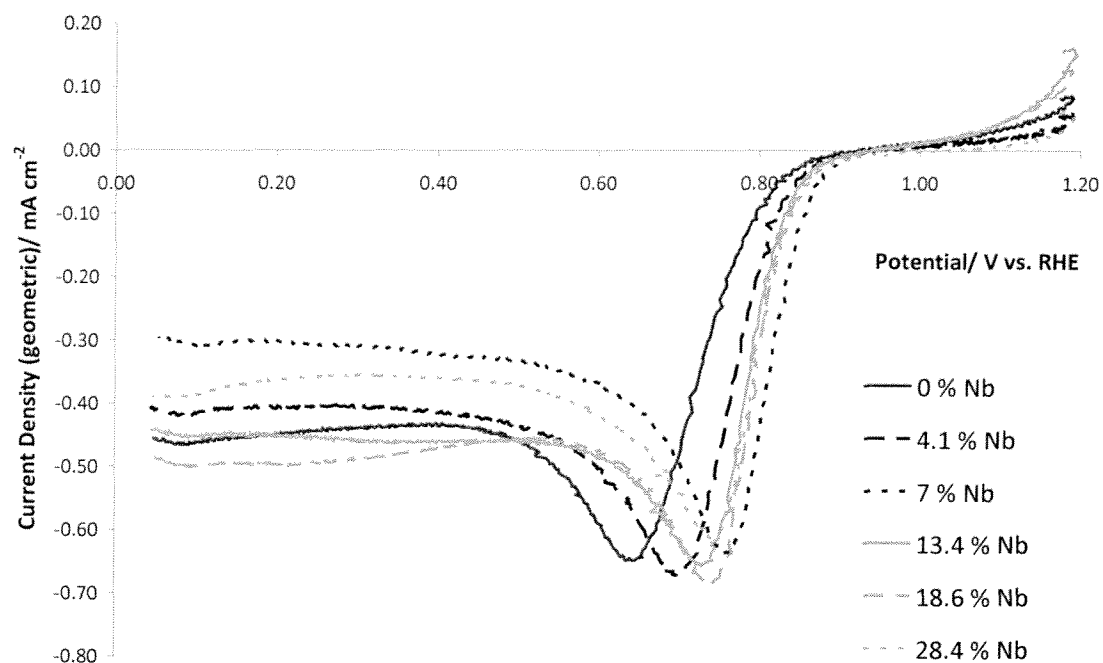


Fig. 20

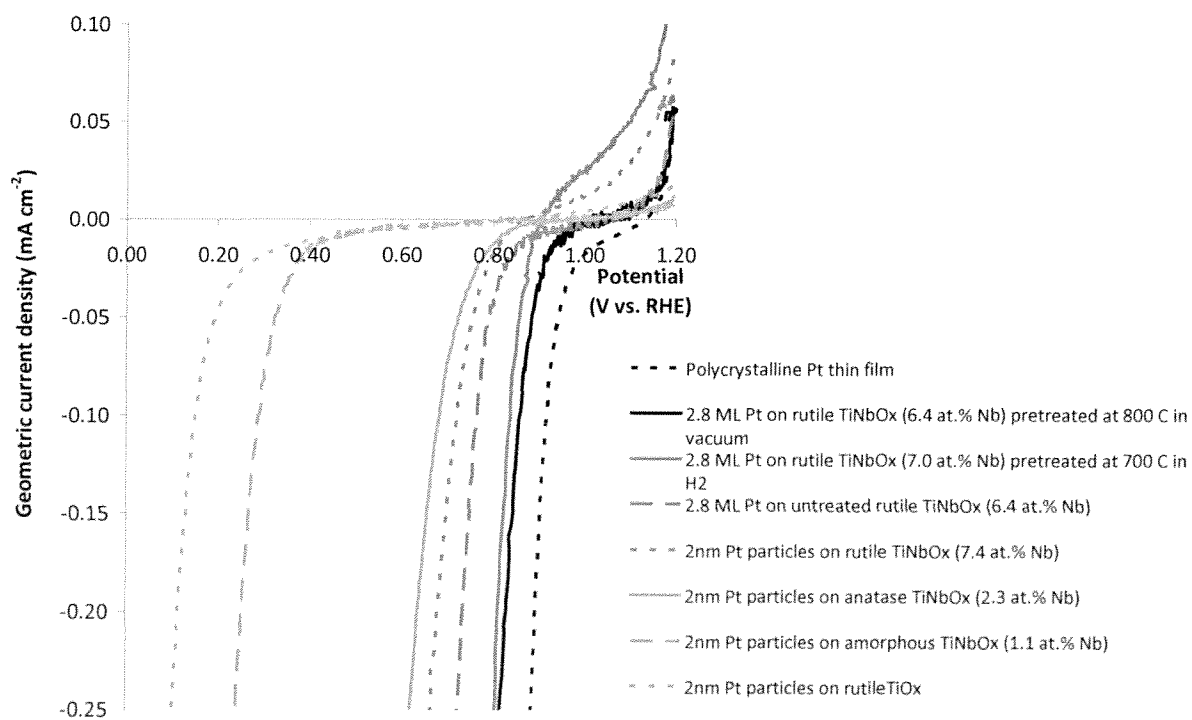


Fig. 21

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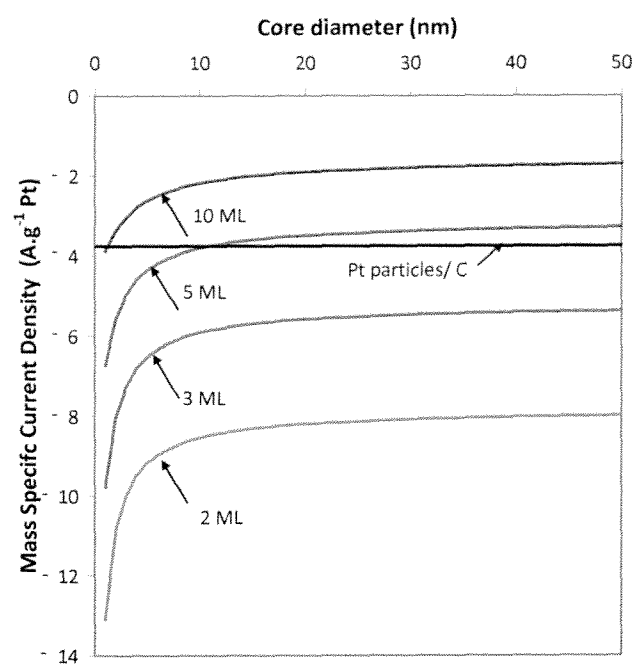


Fig. 22

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/062768

A. CLASSIFICATION OF SUBJECT MATTER INV. B01J21/06 B01J23/42 B01J23/648 B01J37/02 B01J35/00 H01M4/92 H01M8/10 H01M4/86 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) 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 practical, search terms used) EPO-Internal, WPI Data																	
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>US 2009/065738 A1 (WEIDNER JOHN W [US] ET AL) 12 March 2009 (2009-03-12) claims; examples -----</td> <td>1-22</td> </tr> <tr> <td>X</td> <td>US 2007/037041 A1 (CAI MEI [US] ET AL) 15 February 2007 (2007-02-15) claims; examples -----</td> <td>1-22</td> </tr> <tr> <td>X</td> <td>WO 2009/152003 A2 (GM GLOBAL TECH OPERATIONS INC [US]) 17 December 2009 (2009-12-17) claims; examples -----</td> <td>1-22</td> </tr> <tr> <td>X</td> <td>US 2006/263675 A1 (ADZIC RADOSLAV [US] ET AL) 23 November 2006 (2006-11-23) cited in the application claims; examples -----</td> <td>1-22</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	US 2009/065738 A1 (WEIDNER JOHN W [US] ET AL) 12 March 2009 (2009-03-12) claims; examples -----	1-22	X	US 2007/037041 A1 (CAI MEI [US] ET AL) 15 February 2007 (2007-02-15) claims; examples -----	1-22	X	WO 2009/152003 A2 (GM GLOBAL TECH OPERATIONS INC [US]) 17 December 2009 (2009-12-17) claims; examples -----	1-22	X	US 2006/263675 A1 (ADZIC RADOSLAV [US] ET AL) 23 November 2006 (2006-11-23) cited in the application claims; examples -----	1-22
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X	US 2006/263675 A1 (ADZIC RADOSLAV [US] ET AL) 23 November 2006 (2006-11-23) cited in the application claims; examples -----	1-22															
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Date of the actual completion of the international search 10 April 2012		Date of mailing of the international search report 18/04/2012															
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2011/062768

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009065738	A1	12-03-2009	NONE
US 2007037041	A1	15-02-2007	US 2007037041 A1 15-02-2007
		US 2010160153	A1 24-06-2010
WO 2009152003	A2	17-12-2009	US 2009312181 A1 17-12-2009
		WO 2009152003	A2 17-12-2009
US 2006263675	A1	23-11-2006	CA 2607871 A1 23-11-2006
		CN 101180123	A 14-05-2008
		EP 1883468	A2 06-02-2008
		JP 2008545604	A 18-12-2008
		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