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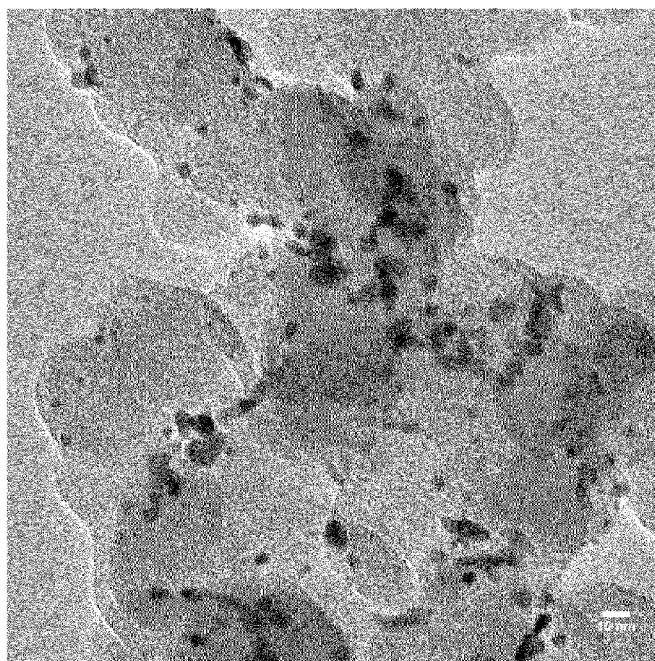
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(54) Title: PROCESS FOR PRODUCING METAL ALLOY NANOPARTICLES



TEM image

(57) **Abstract:** The present invention relates to a process for the production of metal alloy nanoparticles which catalyse the oxygen reduction reaction (ORR) for use in proton exchange membrane fuel cells (PEMFC) or electrolyser cells. In particular, the present invention relates to production of nanoparticles consisting of alloys of a first metal selected from platinum group metals and a second metal suitable for making such alloys. An important feature of the present invention is the use of vaporised alkali metal to promote the reduction of the second metal during the alloying process.



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PROCESS FOR PRODUCING METAL ALLOY NANOPARTICLES

Technical field of the invention

The present invention relates to a process for the production of alloy nanoparticles
5 which catalyse the oxygen reduction reaction (ORR) for use in e.g. proton
exchange membrane fuel cells (PEMFC) or electrolyser cells. In particular, the
present invention relates to production of nanoparticles consisting of alloys of a
first metal which is a platinum group metal and a second alloying metal suitable
for making such alloys. An important feature of the present invention is the use of
10 vaporised alkali metal to promote the reduction of the second alloying metal
during the alloying process.

Background of the invention

Proton exchange membrane fuel cells (PEMFC) are the most common type of fuel
15 cells and the technology rely on the expensive metal platinum as the catalyst for
both the anode and cathode. The platinum is dispersed on a carbon support in the
form of nanoparticles to maximize its surface with respect to its mass. While
rather little platinum is needed for the hydrogen oxidation reaction (HER), the
oxygen reduction reaction (ORR) needs a significant amount of platinum. Thus,
20 the platinum cost can take a significant share in the cost of a fuel cell system,
possibly in excess of 30%.

Different approaches have been undertaken to reduce the amount or eliminate the
need of platinum. It is well-known that higher activity per unit mass can be
25 realized by alloying platinum with late transition metals like nickel and cobalt.
Recent findings suggest that alloying platinum with rare earth metals (RE, i.e.
yttrium, scandium and the lanthanides) results in an even higher increase in
platinum mass activity. However, synthesizing the desired alloy nanoparticles in
the right composition and size is very difficult in a scalable manner. Alloy electro
30 catalysts of platinum and nickel or cobalt are produced and commercially
available.

Both platinum catalysts and platinum alloy catalysts are made by reduction (or co-reduction) of metal salts, but alloys of platinum and e.g. rare earths cannot be manufactured by the same methods. The reason is that rare earths metals are extremely non-noble or electropositive. Consequently, they require very strong
5 reducing agents and the process cannot be carried out in water. Moreover, platinum is so noble that the difference to the rare earths in standard reduction potential is more than 3 V. Co-reduction is difficult because any reducing agent will prefer reducing the platinum ions first and form a core of platinum, possibly with a skin of e.g. rare earth metal on top instead of an alloy.

10

It is possible to alloy platinum and other metals such as rare earths by casting from a furnace with a protected atmosphere, but that will not lead to nanoparticles, not even after milling. Unalloyed nanoparticles of the metals can be alloyed by annealing, but then they also sinter and form larger particles with a
15 lower specific surface area. In summary, there are challenges in respect to alloying very different metals and to do it in the form of nanoparticles.

Thus, *J. S. Kanady et al., J. Am. Chem. Soc., 2017, 139, 5672-5675* discloses a process for producing Pt_xY alloy nanoparticles in the 5 – 20 nm size range. The
20 process requires a high purity environment and molten borohydride salt (MEt_3BH , $M = Na, K$) is used as both the reducing agent and reaction medium. Platinum and yttrium are provided as halide salts of the metals, e.g. $PtCl_4$ and YCl_3 . The grey powder following the reduction step is annealed at 650 °C for 2 hours, and the resulting Pt_xY nanoparticles washed in acid. The described process is thus
25 challenged by the fact that molten borohydride is used for reduction of yttrium. The method requires strict control of the reaction environment, which is a limiting factor for the scalability, and results in nanoparticles with a broad particle size distribution not applicable in PEMFCs.

30 *C. Roy et al., ACS Catal., 2018, 8, 2071-2080* discloses a process for producing Pt_xY alloy nanoparticles, by reduction of YCl_3 using a high flow of hydrogen gas at 800 °C. The use of alkali- or alkaline earth metal vapour is not disclosed, and the process must be kept rigorously free of oxygen and moisture.

WO 2017/191126 discloses a chemical process for preparing nanoparticles of an alloy comprising both a noble metal such as platinum, palladium, gold and mixtures thereof, and a non-noble transition or lanthanide metal, such as yttrium, gadolinium or terbium. The process is carried out by reduction with hydrogen and
5 removal of volatile species in gas form at the reaction temperature.

US 4,812,301 discloses a process for producing oxygen-free titanium carbide, nitride or carbonitride in powder form. The process comprises treating a gas phase mixture of titanium halide, desirably TiCl_4 , a reductant vapour, desirably
10 sodium or magnesium, and a reactive gas capable of furnishing carbon, nitrogen, or mixtures thereof, at a reaction temperature of 500-1250 °C. The disclosure does not relate to alloys of platinum group metals.

Hence, an improved method to reduce the required amount of platinum group
15 metal in the ORR catalysts would be advantageous, and in particular a more efficient and/or reliable process to produce ORR catalyst nanoparticles that are metal alloys of platinum group metals and other alloying metals, would be advantageous. Particularly, scalable processes that are less sensitive to air and moisture for the production of alloy nanoparticles would be desirable.

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Summary of the invention

Thus, an object of the present invention relates to the provision of an improved process for the provision of alloy nanoparticles comprising alloys of platinum group metals.

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In particular, it is an object of the present invention to provide a process for production of alloy particles in the nanometer range that solves the above mentioned problems of the prior art with non-scalable processes that require sensitive reductants and/or rigorous exclusion of moisture and air, and may
30 produce larger than nanoscale particles.

Thus, one aspect of the invention relates to a process for producing alloy nanoparticles, comprising the steps of:

- a) distributing a salt of at least one alloying metal onto a material comprising a platinum group metal, to provide an alloying premixture,
- 5 b) contacting said alloying premixture with an alkali metal vapour or an alkaline earth metal vapour for reducing said alloying metal to provide an alloy precursor,
- c) annealing the alloy precursor by means of heating said alloy precursor to at least 300°C, to produce said alloy nanoparticles,
- 10 wherein said alloying metal is selected from the group consisting of alkaline earth metals, transition metals and lanthanides, or mixtures thereof.

Another aspect of the present invention relates to the use of an alkali metal vapour or alkaline earth metal vapour in the production of alloy nanoparticles for
15 the reduction of a salt of at least one alloying metal in an alloying premixture, said alloying premixture also comprising a platinum group metal.

Brief description of the figures

Figure 1, shows a TEM image of the Pt_xY/C nanoparticles as prepared according to example 3, and reveals that the diameter of the particles is within the 5-15 nm
20 range.

Figure 2, shows a XRD spectrum of the Pt_xY/C nanoparticles, as prepared according to example 1, and reference peaks for metallic platinum, Pt₂Y and Pt₃Y.
25 The figure reveals that the sample consist mostly of Pt₃Y and Pt₂Y, with only small amounts of metallic Pt.

Figure 3, shows a XRD spectrum of the Pt_xZr/C nanoparticles, as prepared according to example 4, and reference peaks for metallic platinum, Pt₃Zr and
30 ZrO₂. The figure reveals that the sample consist mostly of Pt₃Zr and small amounts of ZrO₂.

Figure 4, shows a drawing of the closed compartment with gas flow through enabled used in example 1 for production of Pt_xY/C nanoparticles. The arrows indicate gas inlets and outlets.

- 5 **Figure 5**, shows a drawing of the closed compartment with gas flow through used in example 2 and 3 with a higher control of the metal vapour for production of Pt_xY/C nanoparticles. The arrows indicate gas inlets and outlets.

Figure 6, shows a XPS trace recorded on a sample of Pt_2Y/Pt_3Y nanoparticles produced according to example 2 (upper trace) and reference traces for metallic yttrium (157.45 eV) and Y_2O_3 (155.35 eV). The figure reveals that the electronic state of yttrium is very close to that of metallic yttrium supporting that a phase of Pt_2Y/Pt_3Y alloy is present close enough to the surface of the produced nanoparticles to alter the catalytic properties of the surface platinum.

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Figure 7 shows XRD spectra of Pt_xLa/C nanoparticles formed by annealing and for which the platinum peak shift features correspond to the respective Pt_2La phase.

Figure 8 shows XRD spectra of Pt_xCe/C nanoparticles formed by annealing and for which the platinum peak shift features correspond to the respective Pt_2Ce phase.

Figure 9 shows, XRD spectra of Pt_xGd/C nanoparticles formed by annealing and for which the platinum peak shift features correspond to the respective Pt_2Gd phase.

25

The present invention will now be described in more detail in the following.

Detailed description of the invention

30 Definitions

Prior to discussing the present invention in further details, the following terms and conventions will first be defined:

Alloy nanoparticle

In the present context, an alloy nanoparticle is a small object that behaves as a whole unit and has a diameter in the range of 1–100 nm. The object consists of different metallic elements that have been mixed and heated to high

5 temperatures to create an alloy material having metallic properties.

Alloying metal and salt thereof

In the present context an alloying metal in the broadest sense is any metal capable of forming an alloy with a platinum group metal. Also, in the present

10 context, the salt of the alloying metal is a compound in which the metals are oxidized with either organic and/or inorganic counter-ions and species in which the metals are in a coordination-complex. The term also includes compounds in which the metal is covalently bonded to the rest of the molecule e.g. organometallic compounds.

15

Material comprising a platinum group metal

In the present context, the material comprising a platinum group metal may comprise platinum group metals in the ground state (oxidation state zero) and/or in higher oxidized state. The platinum group metal may be in the form of a salt, or

20 in a coordination complex, or otherwise bonded to an organic part. The material may also comprise a support material in the form of a solid, such as e.g. carbon. The material is typically in particulate form, such as powder form. The platinum group metal may be in the form of nanoparticles.

25 *Alloying premixture*

In the present context an alloying premixture is a mixture comprising at least a salt of an alloying metal as defined above and a material comprising a platinum group metal as defined above. The premixture may comprise further materials, including e.g. a support material.

30

Alloy precursor

In the present context an alloy precursor is the mixture obtained when subjecting the alloying premixture as defined above to an alkali- or alkaline earth metal vapour.

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Alkali metal

In the present context, the term "alkali metal" refers to the group 1 elements: lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs), and francium (Fr).

5

Alkaline earth metal

In the present context, the term "alkaline earth metal" refers to the group 2 elements: beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra).

10

Alkali- or alkaline earth metal vapour

In the present context an alkali- or alkaline earth metal vapour corresponds to any of the alkali or alkaline earth metals in vaporised form. Vaporisation may be provided by adjusting e.g. temperature and pressure to allow said vaporisation from the alkali metal in solid or liquid form. The term vapour may be used interchangeably with the term gas.

15

Annealing

In the present context, annealing is a heat treatment wherein the physical and sometimes chemical properties of a material is altered. Annealing is usually used to induce softness, relieve internal stresses, refine the structure and improve cold working of the material. Controlled temperatures may be necessary to obtain the desired properties.

20

25 *Support material*

In the present context, a support material is a solid usually comprising carbon, alumina and/or silica, and/ other oxides, and to which a catalyst may be affixed. The material should have a high surface to volume ratio and exhibiting very good durability at the temperature needed to obtain the desired catalytic activity. The support may be inert or participate in the catalytic reactions.

30

Rare earth metal (RE)

In the present context, a rare earth metal is an element selected from the group consisting of scandium (Sc), yttrium (Y), and the 15 lanthanides.

35

Transition metal

In the present context, a transition metal is scandium or yttrium, or an element selected from either of groups 4-11 in the periodic system. The entire group of transition metals in the present context consist of: scandium (Sc), titanium (Ti),
5 vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), cobber (Cu), yttrium (Y), zirconium (Zr), niobium (Nb), molybdenum (Mo), technetium (Tc), ruthenium (Ru), rhodium (Rh), palladium (Pd), silver (Ag), hafnium (Hf), tantalum (Ta), tungsten (W), rhenium (Re), osmium (Os), iridium (Ir), platinum (Pt), gold (Au), rutherfordium (Rf), dubnium (Db), seaborgium
10 (Sg), bohrium (Bh), and hassium (Hs).

Catalyst

In the present context, a catalyst is a chemical substance that by its presence is able to increase the reaction rate of a chemical reaction without itself suffering
15 any permanent chemical change.

Dispersion

In the present context, a dispersion is a system comprising at least two phases, wherein one phase is finely dispersed in the other. It may be phases of one
20 material or different materials.

Ultra-sonication

In the present context, ultra-sonication is the irradiation of a liquid sample with ultrasonic (>20 kHz) waves resulting in agitation. Sound waves propagate into the
25 liquid media and result in alternating high-pressure (compression) and low-pressure (rarefaction) cycles. During rarefaction, high-intensity sonic waves create small vacuum bubbles or voids in the liquid, which then collapse violently (cavitation) during compression, creating very high local temperatures.

Decantation

In the present context, decantation is a process in which a liquid is poured from a solid sediment.

Inert gas

In the present context, an inert gas consists of one or several elements or molecules that are all unreactive under the applied reaction conditions. Most commonly used inert gasses are argon, nitrogen and helium.

5

One-pot

In the present context, one-pot refer to a procedure in which one or several chemical reactions are performed in the same reactor.

10 The process

The present inventors have developed a process which surprisingly allows for facile, scalable and efficient production of alloy nanoparticles of particularly platinum group metals with a broad range of other metals. The process involves mixing a salt or complex of an alloying metal with a material comprising a

15 platinum group metal, in the presence of an alkali- or alkaline earth metal vapour and subsequent or simultaneous annealing of the metal salt and the platinum group metal at high temperature. The process facilitates the production of efficient platinum group metal-metal alloys with good catalytic efficiency, and consequently allows for a reduced use of the very expensive platinum group
20 metals, without compromising efficiency. The alloy particles formed are in the nano-scale, which is an advantage as that e.g. improves catalytic performance.

Therefore, a first aspect of the present invention is a process for producing alloy nanoparticles, comprising the steps of:

- 25 a) distributing a salt of at least one alloying metal onto a material comprising a platinum group metal, to provide an alloying premixture,
b) contacting said alloying premixture with an alkali metal vapour or an alkaline earth metal vapour for reducing said alloying metal to provide an alloy precursor,
30 c) annealing the alloy precursor by means of heating said alloy precursor to at least 300°C, to produce said alloy nanoparticles

wherein said alloying metal is selected from the group consisting of alkaline earth metals, transition metals and lanthanides, or mixtures thereof.

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The alloying metal and salts thereof

In the context of the present invention, the alloying metal is selected from the group consisting of alkaline earth metals, transition metals and lanthanides, or
5 mixtures thereof. preferably the alloying metal is selected from the group consisting of rare earth metals and early transition metals, or mixtures thereof. Rare earth metals are especially preferred, and they result in good catalytic activity of the resulting alloy.

- 10 The alkaline earth metals may be selected from the group consisting of beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), radium (Ra). calcium is preferred.

- The transition metal may be selected from the group consisting of scandium (Sc),
15 titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), cobber (Cu), yttrium (Y), zirconium (Zr), niobium (Nb), molybdenum (Mo), technetium (Tc), ruthenium (Ru), rhodium (Rh), palladium (Pd), silver (Ag), hafnium (Hf), tantalum (Ta), tungsten (W), rhenium (Re), osmium (Os), iridium (Ir), platinum (Pt), gold (Au), rutherfordium (Rf), dubnium
20 (Db), seaborgium (Sg), bohrium (Bh), and hassium (Hs). Preferably the transition metal is selected from the group consisting of titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), zirconium (Zr), niobium (Nb), molybdenum (Mo), hafnium (Hf), tantalum (Ta), tungsten (W) and rhenium (Re).

- The lanthanides may be selected from the group consisting of Lanthanum (La),
25 Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Promethium (Pm), Samarium (Sm), Europium (Eu), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), Ytterbium (Yb), and Lutetium (Lu).

- Preferably the rare earth metal is selected from the group consisting of cerium
30 (Ce), dysprosium (Dy), erbium (Er), europium (Eu), gadolinium (Gd), holmium (Ho), lanthanum (La), lutetium (Lu), neodymium (Nd), praseodymium (Pr), samarium (Sm), scandium (Sc), terbium (Tb), thulium (Tm), ytterbium (Yb), and yttrium (Y).

In one particular embodiment the alloying metal is selected from the group consisting of yttrium, and zirconium, or mixtures thereof. Further, in one embodiment the alloying metal is not iron (Fe) or a salt thereof.

- 5 The salt of the at least one alloying metal may preferably be selected from the group consisting of YCl_3 , YBr_3 , YI_3 , ScCl_3 , ScBr_3 , ScI_3 , GdCl_3 , GdBr_3 , GdI_3 , LaCl_3 , CeCl_3 , ZrCl_4 , ZrOCl , and mixtures or hydrates thereof.

The present inventors have found that increasing the amount of the salt of the
 10 alloying metal may help to control particle growth and promote the formation of alloy nanoparticles rather than larger particles. Thus, in a preferred embodiment the alloying metal is present in a molar excess as compared to the platinum group metal, such as in a platinum group metal to alloying metal molar ratio of 1:1.1, such as 1:2, 1:3, 1:5, or 1:10.

15

The material comprising a platinum group metal

The material comprising a platinum group metal may be either a metal as such, possibly in nanoparticle form, or a salt of the metal, or the metal mixed with a support material. Thus, in a preferred embodiment the material comprising a
 20 platinum group metal is selected from the group consisting of a platinum group metal, a salt of a platinum group metal, and particles of a platinum group metal on a support material. In some embodiments a support material may be added separately. Hence a combination of a salt of a platinum group metal and a separately added support material may for example be used.

- 25 The second metal, which is combined in the alloy with the alloying metal is a platinum group metal and may be selected from the group consisting of ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt), preferably platinum (Pt). The salt of a platinum group metal may be selected from the group consisting of H_2PtCl_6 , PtCl_2 , PtI_2 , PtBr_2 , $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$, and
 30 mixture or hydrates thereof.

The support material, whether it is added with platinum group metal nanoparticles or separately may be based on materials selected from the group consisting of carbon, alumina, silica, titanium oxide, or combinations thereof. The material

comprising platinum group metal on a support may thus preferably be platinum group metal on carbon, such as preferably platinum on carbon (Pt/C).

The platinum group metal may be in the form of particles preferably platinum group metal nanoparticles, such as platinum nanoparticles.

In preferred embodiments the nanoparticles of the platinum group metal on a support material comprises 10-90% of platinum group metal, such as 15-80%, 15-60%, such as preferably 15-45% platinum group metal.

10

The alkali- or alkaline earth metal for vaporisation

The alkali metal vapour or alkaline earth metal vapour as provided in the process of the present invention is a strong reductant and promotes the reduction of the alloying metal salt or complex to the metallic form (oxidation state zero), which may then participate in the formation of the alloy nanoparticles.

Preferably, the alkali metal or alkaline earth metal is selected from the group consisting of lithium (Li), sodium (Na), potassium (K), and magnesium (Mg), and calcium (Ca), more preferably the group consisting of sodium (Na) and potassium (K), most preferably potassium (K).

The alloy nanoparticles

The alloy nanoparticles of the present invention may be provided in crude form or they may be purified further prior to use, e.g. with acid leaching and/or washing with water as further described below. This typically will depend on the initial purity of the crude alloy nanoparticles. It should be understood that when referring to alloy nanoparticles, these particles may be present in conjunction with said support material. The alloy nanoparticles may preferably have an average particle size of 1-100 nm, such as preferably 1-40 nm, 1-20 nm, such as 1-15 nm. The alloy nanoparticle preferably have catalytic activity, particularly in an oxygen reduction reaction (ORR) of, e.g. a fuel cell. Therefore, the alloy nanoparticles are preferably a catalyst, such as a catalyst for the ORR reaction.

The alloy nanoparticles are an alloy of the first metal (M) and the second metal, which is a platinum group metal (Px), and thus the alloy nanoparticles may

comprise an alloy in the form of $Px_n(M)_m$, wherein n is 2, 3, 4, 5, 6, 7, 8, 9 or 10 and m is 1, 2 or 3, wherein Px represents any platinum group metal, preferably platinum, and wherein M represents the alloying metal. Preferably, the alloy nanoparticles comprise $Px_n(M)_m$, wherein n is 2, 3, 4, or 5 and m is 1, 2 or 3.

5

In a particularly preferred embodiment, the alloy nanoparticles comprise an alloy selected from the group consisting of Pt_2Y , Pt_3Y , Pt_3Zr , Pt_2Gd , Pt_3Gd , Pt_5Gd , Pt_2Tb , Pt_3Tb , Pt_5Tb , Pt_2La , and Pt_2Ce . The nanoparticles are preferably supported on carbon.

10

Process steps and further parameters

The process of the present invention comprises three primary steps [steps a), b) and step c)]. Step a) involves the mixing of a salt of an alloying metal with a material comprising a platinum group metal, where the two metals eventually
15 form the alloy particles, in order to form an alloying premixture. Step b) involves contacting the alloying premixture with a alkali metal or alkaline earth metal vapour, in order to reduce the salt(s) of the alloying metal used. Alkali- or alkaline earth metal vapour is a strong reductant in gas form. Step b) forms an alloy precursor. Step c) is an annealing step, which involves the heating of the alloy
20 precursor to form alloy nanoparticles. It is important to note that the method of the present invention may comprise additional steps before step a), in between step a) and step b), in between step b) and step c) and finally also after step c). Thus, further details regarding steps a), b) and c) and additional steps of the present invention are described in the following. Also, steps b) and c) may
25 effectively be carried out in straight succession or simultaneously, i.e. by continuously heating a compartment comprising both an alkali metal and the alloying premixture to eventually form the alloy nanoparticles via the alloy precursor.

30 In a particular embodiment the distribution of the salt of at least one alloying metal onto the material comprising platinum group metal of step a) is performed by creating a dispersion of said alloying metal and said material comprising platinum group metal in a solvent and then removing the solvent to form the alloying premixture. The solvent may preferably be selected from the list
35 consisting of water, ethers, alkanes, alcohols, halogenated alkanes and

acetonitrile. Such solvents may be a solvent is selected from the list consisting of water, tetrahydrofuran, dioxane, diethyl ether, pentane, hexane, heptane, methanol, ethanol, 1-propanol, and 2-propanol. The dispersion may be created by ultra-sonication in e.g. a water bath for 5 min-10 hours, such as 5 min-5 hours, 5 min-2 hours, such as preferably 5 min – 1 hour.

The solvent is preferably removed before proceeding to step b). The solvent may be removed by evaporation. Alternatively, the solvent may be removed by centrifugation of the dispersion for 1-30 min, such as 5-15 min, such as preferably 10 min, followed by decantation of the separated solvent. Finally the solvent may also be removed by vacuum filtration.

A drying step after step a) may also be used, so in one embodiment the alloying premixture of step a) is dried in an oven at a temperature such as 20-110 °C, 50-110 °C, 70-110 °C, such as preferably 80-110 °C. Also, the alloying premixture provided in step a) may be mortared.

Depending on the process parameters and the desired composition of the resulting alloy nanoparticles the atomic ratio of the two metals that form the alloy may be varied. Hence, the atomic ratio of alloying metal to platinum group metal in the alloying premixture may be 8:1-1:30, 2:1-1:10, such as preferably 1:1-1:5. Atomic ratio may also be referred to as molar ratio.

The alloying premixture may in certain embodiments comprise an inorganic salt, such as preferably KCl or NH₄Cl. Its purpose may be minimizing particle growth during annealing step by acting as spacer or by transforming a present hydrated metal salt into its anhydrous form. Said inorganic salt will be removed in the washing step or simply by sublimation or decomposition during the annealing step.

30

The reduction of step b) may advantageously be performed under the controlled conditions attainable in a closed compartment adapted to provide a flow through of gas. Hence, in one embodiment the reduction of the salt of an alloying metal in the alloying premixture of step b) is performed in a closed compartment, preferably adapted to provide a flow of gas. The closed compartment may be an

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alumina tube. The closed compartment may preferably be adapted to position in a furnace.

The alkali or alkaline earth metal vapour of step b) may be attained by subjecting
5 a solid alkali or alkaline earth metal or a liquid eutectic mixture of alkali metal, such as NaK to e.g. an increase in temperature and/or a decrease in pressure. Preferably the vapour is provided by increasing the temperature, and thus in a preferred embodiment the alkali- or alkaline earth metal vapour of step b) is provided by vaporisation of the alkali metal at a temperature such as 250-500 °C,
10 300-500 °C, such as preferably 350-400 °C, such as preferably 400-500 °C.

The alkali or alkaline earth metal may be positioned in the same compartment as the alloying premixture, and the vapour formed when raising the temperature towards the final annealing temperature, or in an alternative embodiment the
15 alkali or alkaline earth metal may be positioned in a separate compartment and the alkali or alkaline earth metal formed there, where after the vapour is transferred to the compartment comprising the precursor mixture. The latter embodiment allows for the use of different temperatures and/or pressures for vapour formation and annealing/alloy formation (steps b) and c) respectively).
20 The alkali- or alkaline earth metal vapour of step b) may be provided by vaporisation for a duration such as 0.5-6 hours, 1-5 hours, such as preferably 1-3 hours.

The reduction of step b) is preferably performed under a stream of gas at a
25 flowrate such as 10-200 ml/min, 15-100 ml/min, such as preferably 20-50 ml/min. The gas stream helps to bring the evaporated alkali or alkaline earth metal into contact with the alloying premixture. Preferably the gas comprises or consists of an inert gas. The inert gas may nitrogen or argon. In some embodiments the gas may comprise hydrogen and an inert gas. Preferably the
30 gas would then comprise 1-10% (V/V) hydrogen, such as about 5% (V/V) hydrogen gas.

Step c) involves the heating the alloy precursor obtained by contacting the alloying premixture with the alkali- or alkaline earth metal vapour. The annealing
35 process of step c) may be performed at a temperature such as 150-1200 °C, 200-

1000 °C, 300-700 °C, such as preferably 350-600 °C. Preferably the annealing process of step c) is performed for a duration of 0.5-6 hours, such as 1-6 hours, such as preferably 1-2 hours.

- 5 Further isolation and purification of the resulting alloy nanoparticles of step c) may or may not be necessary depending on the particular process used. Upon completion of the annealing of step c), the sample may be cooled, and water may be added to neutralise any remaining alkali- or alkaline earth metal vapour. In certain embodiments the alloy nanoparticles provided in step c), are washed in a
- 10 solution comprising an inorganic acid, preferably at an acid concentration such as 0.1-5.0 M, 0.1-0.5, such as preferably 0.1-0.2 M. The inorganic acid may be selected from the group consisting of sulphuric acid (H_2SO_4), hydrochloric acid (HCl), hydrofluoric acid (HF), nitric acid (HNO_3) and phosphoric acid (H_3PO_4), preferably sulphuric acid (H_2SO_4). The acid wash may be followed by filtration to
- 15 remove oxides dissolved in the acid. The alloy nanoparticles provided in step c) may also be washed with a further acid and/or water, preferably purified water, even more preferably deionized water or milliQ water. Finally, the alloy nanoparticles provided in step c) may be dried in an oven at a temperature such as 20-110 °C, 50-110 °C, such as preferably 105-110 °C.

20

- It is to be understood that the reduction of step b) and the annealing of step c) may be performed in the same compartment in direct succession of each other and even simultaneously, at least in part. This essentially corresponds to performing the step in one-pot, although the alkali metal in its solid form prior to
- 25 vaporisation may be positioned separately from the alloying premixture. In this scenario, as the temperature is raised, the annealing may begin prior to the alkali metal has been fully vaporized. Thus, in a preferred embodiment steps b) and c) are performed in one-pot, i.e. in direct succession and/or partly simultaneously. The temperature during one-pot reduction and annealing may be in the range of
- 30 200 - 600 °C, such as 300 - 500 °C, such as preferably around 350 °C. The one-pot reduction and annealing step may have a duration of 0.5-6 hours, such as 1-5 hours, such as preferably 1-3 hours.

- As mentioned, the present invention allows for relaxation of the requirement of
- 35 oxygen and moisture free environments, and thus a preferred process of the

invention is a process wherein no steps of the process are performed in a glove box.

In a particularly preferred embodiment, the alloy nanoparticles of the present invention are for use in a proton exchange membrane fuel cell (PEMFC), or an electrolyzer cell.

Some particular preferred embodiments of the present invention include:

10 A process for producing alloy nanoparticles, comprising the steps of:

- a) distributing a salt of at least one alloying metal onto a material comprising a platinum group metal, to provide an alloying premixture,
- b) contacting said alloying premixture with an alkali metal vapour or an alkaline earth metal vapour for reducing said alloying metal to provide an alloy precursor,

15

- c) annealing the alloy precursor by means of heating said alloy precursor to at least 300°C, to produce said alloy nanoparticles

wherein said alloying metal is selected from the group consisting of alkaline earth metals, transition metals and lanthanides, or mixtures thereof, and

20 wherein said platinum group metal is selected from the group consisting of ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt), and

wherein said alkali- or alkaline earth metal is selected from the group consisting of lithium (Li), sodium (Na), potassium (K), magnesium (Mg), and calcium (Ca).

25

A process for producing alloy nanoparticles, comprising the steps of:

- a) distributing a salt of at least one alloying metal onto a material comprising a platinum group metal, to provide an alloying premixture,
- b) contacting said alloying premixture with an alkali metal vapour or an alkaline earth metal vapour for reducing said alloying metal to provide an alloy precursor,

30

- c) annealing the alloy precursor by means of heating said alloy precursor to at least 300°C, to produce said alloy nanoparticles

wherein said alloying metal is a rare earth metal, and

wherein the alkali-metal vapour or alkaline earth metal vapour of step b) is provided by vaporisation of the alkali metal or alkaline earth metal at a temperature such as 250-500 °C.

5 A process for producing alloy nanoparticles, comprising the steps of:

a) distributing a salt of at least one alloying metal onto a material comprising a platinum group metal, to provide an alloying premixture,

b) contacting said alloying premixture with an alkali metal vapour for reducing said alloying metal to provide an alloy precursor,

10 c) annealing the alloy precursor by means of heating said alloy precursor to at least 300°C, to produce said alloy nanoparticles

wherein said alloying metal is a rare earth metal selected from the group consisting of cerium (Ce), dysprosium (Dy), erbium (Er), europium (Eu), gadolinium (Gd), holmium (Ho), lanthanum (La), lutetium (Lu), neodymium (Nd),
15 praseodymium (Pr), samarium (Sm), scandium (Sc), terbium (Tb), thulium (Tm), ytterbium (Yb), and yttrium (Y), and

wherein said platinum group metal is selected from the group consisting of ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt), and

20 wherein said alkali metal is selected from the group consisting of sodium (Na) and potassium (K).

Another aspect of the present invention is an alloy nanoparticle obtainable by the method according to the first aspect as described above.

25

Yet another aspect of the present invention is the use of an alkali- or alkaline earth metal vapour in the production of alloy nanoparticles for the reduction of a salt of at least one alloying metal in an alloying premixture, said alloying premixture also comprising a platinum group metal.

30

The embodiments relating to the process of the first aspect also applies to the second use aspect. Particularly, the alloying metal may be selected from the group consisting of alkaline earth metals, transition metals and lanthanides, or mixtures thereof. Preferably the alloying metal may be a rare earth metal, or a
35 mixture hereof. The alkali metal may also be selected from the group consisting

of, sodium (Na) and potassium (K), preferably potassium (K). Also, the platinum group metal is selected from the group consisting of ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt), preferably platinum (Pt). Finally, the alloy nanoparticles may be for use in a proton exchange
5 membrane fuel cell (PEMFC) or an electrolyser cell.

It should be noted that embodiments and features described in the context of one of the aspects of the present invention also apply to the other aspects of the invention.

10

All patent and non-patent references cited in the present application, are hereby incorporated by reference in their entirety.

The invention will now be described in further details in the following non-limiting
15 examples.

Examples

Materials

- yttrium(III)chloride (YCl_3), LaCl_3 , CeCl_3 , and GdCl_3 were sourced from Sigma
20 Aldrich
- Pt/C
- Pt/C (40%, HiSpec4000) sourced from Johnson Matthey
- hexane sourced from Sigma Aldrich
- potassium metal sourced from Sigma Aldrich
- 25 - 5% hydrogen in argon gas ($\text{H}_2\text{Ar-5}$) from AGA
- sulphuric acid (H_2SO_4) sourced from Sigma Aldrich
- $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ sourced from Sigma Aldrich
- NH_4Cl sourced from Sigma Aldrich
- Hydrofluoric acid (HF) sourced from Alfa Aesar
- 30 - zirconium(IV)chloride (ZrCl_4).

Instrumentation

Powder X-ray diffraction (XRD) measurements were performed with a MiniFlex 600 X-ray diffractometer (Rigaku) using a Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation source.

Transmission electron microscope (TEM) images were obtained with an FEI Titan Analytical 80-300ST TEM equipped with a spherical aberration corrector and a X-Max TLE Energy Dispersive X-Ray Spectroscopy (EDS) detector at 300 kV. X-ray photoelectron spectroscopy (XPS) was done on a Thermo Scientific™ K-Alpha+™ X-ray Photoelectron Spectrometer with an A1 K(α) X-ray monochromator.

Example 1 - Process A for preparation of Pt_xY/C

- a)** 400 mg of mortared yttrium(III)chloride (YCl₃) and 100 mg Pt/C is filled into a centrifuge tube. 50 ml hexane is added and the centrifuge tube is closed and shaken. The tube is ultra-sonicated in a water bath for 10 hours. The tube is centrifuged at 9000 rpm for 10 min and the black dispersion separated into a clear liquid and black solid phase. The clear liquid phase is discarded and the black solid premixture is dried in vacuum for 1 hour.
- b)** The premixture sample is placed in an alumina boat which is put into a long quartz tube on top of another alumina boat containing 50 mg of freshly cut potassium metal as depicted in Figure 4. The quartz tube is closed with quartz caps, with valves attached at the end. The closed quartz tube is transferred to a tube furnace and 5% hydrogen in argon gas (H₂Ar-5) is connected to the inlet valve of the quartz tube. Before starting the gas flow, the gas lines are evacuated and eventually the inlet and outlet valves are opened to allow a constant flow of H₂Ar-5 through the quartz tube and over the sample. Now an annealing program is started maintaining 600 °C for 30 min. Potassium metal is thus vaporised and contacted with the premixture to form the alloy precursor, which further undergoes annealing.
- c)** The quartz tube is allowed to cool down and the sample is transferred into a new centrifuge tube. The tube is carefully opened and 40 ml of deionized water is (alternatively ethanol for larger batches) is quickly filled into it to neutralize the remaining evaporated and condensed potassium.
- 2c)** The sample is filled into a bottle with 500 ml of 0.1 M sulphuric acid (H₂SO₄) and shaken. The resulting black dispersion is vacuum filtered to remove leftover YCl₃ and Y₂O₃ from the sample. Deionized water is used to remove last traces of sulphuric acid from the filter cake. The filter and the filter cake are placed in a petri dish and set to dry in an oven at 110 °C, to obtain alloy nanoparticles.

Example 2 - Process B for preparation of Pt_xY/C

- a)** 600 mg YCl₃·6H₂O and 1000 mg NH₄Cl are dissolved in 3.5 ml water. 100 mg Pt/C (40%) is added to the solution and ultra-sonicated for 5 minutes. The dispersion is placed in an oven at 110 °C to let the water evaporate. The remaining solid is collected and mortared until a homogeneous black powder is collected as the alloying premixture.
- b)** 200 mg of the powder is placed in alumina crucible A. 200 mg of freshly cut potassium is placed in another alumina crucible, crucible B. Crucible B is placed in zone 1 of a multi-heating zone tube furnace as depicted in Figure 5, using an alumina tube. Crucible A is placed in zone 3. The tube furnace is flushed with argon gas at 0.5 l/min with a flow direction from zone 1, through zone 2, and into zone 3. Zone 3 is heated to 150 °C for 1 hour and then 400 °C for 4 hours, while zone 1 is set to 50 °C. Zone 3 is finally heated to 600 °C while zone 1 is heated to 490 °C, both for 30 min. The powder from crucible A is collected and washed as described in example 1, step 2c to obtain alloy nanoparticles.

Example 3 - Process C for preparation of Pt_xY/C

- a)** 4 g of YCl₃·6H₂O is dissolved in 5 ml deionized water. 200 mg of Pt/C (40%, HiSpec4000) is dispersed in the yttrium chloride solution using ultra-sonication for at least 30 min. The resulting dispersion is vacuum filtered and the filter cake is dried at 105 °C in air and mortared to a fine powder, which is the alloying premixture.
- b)** Annealing the precursor under a potassium vapour and argon atmosphere at 350 °C for 6 hours, in a furnace.
- c)** collecting the sample and washing it with 0.1 M sulphuric acid and deionized water. The sample is subsequently dried at 105 °C in air to obtain the final to obtain alloy nanoparticles.

Example 4 - Process B for preparation of Pt_xZr/C

The same procedure is used as described for preparation of Pt_xY in example 1. However, the powder comprising alloy nanoparticles is collected and washed as described in step 2c, except for the following change. After the sulphuric acid

wash, the dried filter cake is scraped off the filter and dispersed in 200 ml of 10% hydrofluoric acid (HF) and stored under stirring for 10 hours.

Example 5 – Preparation of Pt_xLa, Pt_xCe, and Pt_xGd

- 5 Preparation of Pt_xLa, Pt_xCe, and Pt_xGd nanoparticles is achieved by annealing of Pt/C with salts of LaCl₃, CeCl₃, and GdCl₃, respectively and otherwise following the general procedure outlined in example 1.

Example 6 - Characterization of the products

- 10 The size of the produced Pt_xY/C nanoparticles is an important parameter when creating a catalyst as smaller particles have a higher surface-to-volume ratio and as the catalytic activity usually depend on the surface area. A tunnelling electron microscope (TEM) image of the Pt_xY/C nanoparticles produced as described in example 3 is depicted in Figure 1 and shows that the size of the particles are
15 within the 5-15 nm range.

Information about the chemical composition of the Pt_xY/C nanoparticles produced according to example 1, has been obtained using X-ray diffraction (XRD). An X-ray source is directed onto the sample of nanoparticles. The intensity of the
20 scattered X-ray is recorded as the sample and the detector is rotated, hence the angle of 2Theta in Figures 2 and 3. The exact scattering of the X-ray beam is depending on the crystal structure within the sample material. The lines in the figure is the recorded intensity of the X-ray beam as it is scattered by the nanoparticles. The reference spectre for pure metallic platinum, Pt₂Y, and Pt₃Y
25 (lines in Figure 2) make it possible to collate the peaks on the black line with the signals obtained for each of the references, thus to determine the composition of the nanoparticles. The XRD-spectrum in Figure 2 reveals that the Pt_xY/C nanoparticles consist mostly of Pt₃Y and Pt₂Y, with only small or no amounts of metallic platinum.

30

The characteristics of the Pt_xZr nanoparticles produced as described in example 4, were also investigated with X-ray diffraction measurements. XRD traces for the sample of nanoparticles and the commercial Pt/C catalyst are depicted in Figure 3, alongside reference peaks for metallic platinum, Pt₃Zr, and ZrO₂. The trace signal
35 for the sample is left-shifted from the trace recorded on the commercial Pt/C

catalyst, and thus correlate better with the reference signal for Pt_3Zr , than for metallic Pt. The symmetric bell-shape of the peaks formed by the trace recorded on the sample indicate that Pt_3Zr is the major component in the sample, as visible broadening of the peaks would be expected if metallic platinum was also a major component. It is therefore safe to assume that the nanoparticles consist of Pt_3Zr . Figure 3 also show that the ZrO_2 could not be removed completely during the washing step. It is therefore likely that the nanoparticles should be washed several times, if a clean sample of Pt_3Zr is needed.

X-ray photoelectron spectroscopy (XPS) was used to obtain information about the surface composition of the $\text{Pt}_2\text{Y}/\text{Pt}_3\text{Y}$ nanoparticles. In XPS measurements, the material to be analyzed is irradiated with a beam of X-rays that cause electrons in the surface of the material to escape. Measuring the number of escaping electrons and their energy, provide information about the electronic states of the elements comprising the material. A XPS trace recorded on a sample of $\text{Pt}_2\text{Y}/\text{Pt}_3\text{Y}$ nanoparticles produced according to example 2 (upper trace) and reference traces for metallic yttrium (157.45 eV) and Y_2O_3 (155.35 eV) are provided in Figure 6. It is seen that the electronic state of yttrium is very close to that of metallic yttrium, which shows that an alloy phase of $\text{Pt}_2\text{Y}/\text{Pt}_3\text{Y}$ is present close enough to the surface of the nanoparticles to alter the catalytic properties of the surface platinum. The figure also reveals that about 60% of the yttrium signal belongs to Y_2O_3 , which is not unexpected because yttrium can be easily oxidized and might form some oxide within the carbon where it is protected from dissolving during washing with acid.

The characteristics of Pt_xLa nanoparticles produced as described in Example 5 with 3 hours of annealing and under argon gas, were also investigated using XRD. Two traces were recorded, one wherein washing step 2c was unchanged and a second wherein only water was used. The recorded XRD traces are depicted in Figure 7 alongside reference lines for pure metallic platinum, Pt_2La , and La_2O_3 . The figure illustrates that acid washing is effective at removing La_2O_3 salt from a sample.

The characteristics of Pt_xCe nanoparticles produced as described in Example 5 with 3 hours of annealing and under $\text{H}_2\text{Ar}-5$ gas, were also investigated using XRD. Four traces were recorded wherein the annealing temperature was 300, 350,

400, and 450 °C, respectively. These are depicted in Figure 8 alongside reference lines for pure metallic platinum, Pt₂Ce, and CeO₂. The figure shows that Pt_xCe nanoparticles are formed, especially when the annealing temperature is around 450 °C. Two additional experiments were performed at 450 °C and their
5 respective XRD traces included in Figure 8 (traces in the top). In a first experiment the annealing was performed in H₂Ar-5 gas and without any alkali metal vapour present (no NaK), whereas in a second experiment the alloy precursor was annealed under argon gas and in the presence of alkali metal vapour. Comparison between the traces in Figure 8, shows that annealing of Pt/C
10 with CeCl₃ in a combination of H₂Ar-5 gas and alkali metal vapour is especially advantageous.

Characteristics of Pt_xGd nanoparticles produced as described in Example 5 with 3 hours of annealing and under argon gas, were also investigated using XRD. The
15 traces depicted in Figure 9 confirm that Pt_xGd nanoparticles are formed especially when the annealing temperature is around 450 °C.

References

- J. S. Kanady et al., J. Am. Chem. Soc., 2017, 139, 5672-5675
- C. Roy et al., ACS Catal., 2018, 8, 2071-2080
- WO 2017/191126
- US 4812301

Claims

1. A process for producing alloy nanoparticles, comprising the steps of:
 - a) distributing a salt of at least one alloying metal onto a material comprising a platinum group metal, to provide an alloying premixture,
 - 5 b) contacting said alloying premixture with an alkali metal vapour or an alkaline earth metal vapour for reducing said alloying metal to provide an alloy precursor,
 - c) annealing the alloy precursor by means of heating said alloy precursor to at least 300°C, to produce said alloy nanoparticles,
- 10 wherein said alloying metal is selected from the group consisting of alkaline earth metals, transition metals and lanthanides, or mixtures thereof.
2. The process according to claim 1, wherein the alloying metal is selected from the group consisting of rare earth metals and early transition metals, or mixtures
- 15 thereof.
3. The process according to any one of the preceding claims, wherein the alloying metal is a rare earth metal, or a mixture thereof.
- 20 4. The process according to any one of claims 2 to 3, wherein the rare earth metal is selected from the group consisting of cerium (Ce), dysprosium (Dy), erbium (Er), europium (Eu), gadolinium (Gd), holmium (Ho), lanthanum (La), lutetium (Lu), neodymium (Nd), praseodymium (Pr), samarium (Sm), scandium (Sc), terbium (Tb), thulium (Tm), ytterbium (Yb), and yttrium (Y).
- 25 5. The process according to claim 1, wherein the salt of at least one alloying metal is selected from the group consisting of YCl₃, YBr₃, YI₃, ScCl₃, ScBr₃, ScI₃, GdCl₃, GdBr₃, GdI₃, LaCl₃, CeCl₃, ZrCl₄, ZrOCl, and mixtures or hydrates thereof.
- 30 6. The process according to any one of the preceding claims, wherein the material comprising a platinum group metal is selected from the group consisting of a platinum group metal, a salt of a platinum group metal, and particles of a platinum group metal on a support material.

7. The process according to any one of the preceding claims, wherein the platinum group metal is selected from the group consisting of ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), and platinum (Pt), preferably platinum (Pt).

5

8. The process according to any one of the preceding claims, wherein the material comprising a platinum group metal comprises a support selected from the group consisting of carbon, alumina, silica, titanium oxide, or combinations thereof.

10 9. The process according to any one of the preceding claims, wherein the alkali metal or alkaline earth metal is selected from the group consisting of lithium (Li), sodium (Na), potassium (K), magnesium (Mg), and calcium (Ca).

10. The process according to any one of the preceding claims, wherein the
15 distribution of the salt of at least one alloying metal onto the material comprising platinum group metal of step a) is performed by creating a dispersion of said alloying metal and said material comprising platinum group metal in a solvent and then removing the solvent to form the alloying premixture.

20 11. The process according to any one of the preceding claims, wherein the solvent is selected from the list consisting of water, ethers, alkanes, alcohols, halogenated alkanes, and acetonitrile.

12. The process according to any one of the preceding claims, wherein the alkali
25 metal vapour or alkaline earth metal vapour of step b) is provided by vaporisation of said metal at a temperature such as 250-500 °C, 300-500 °C, such as preferably 350-400 °C, such as preferably 400-500 °C.

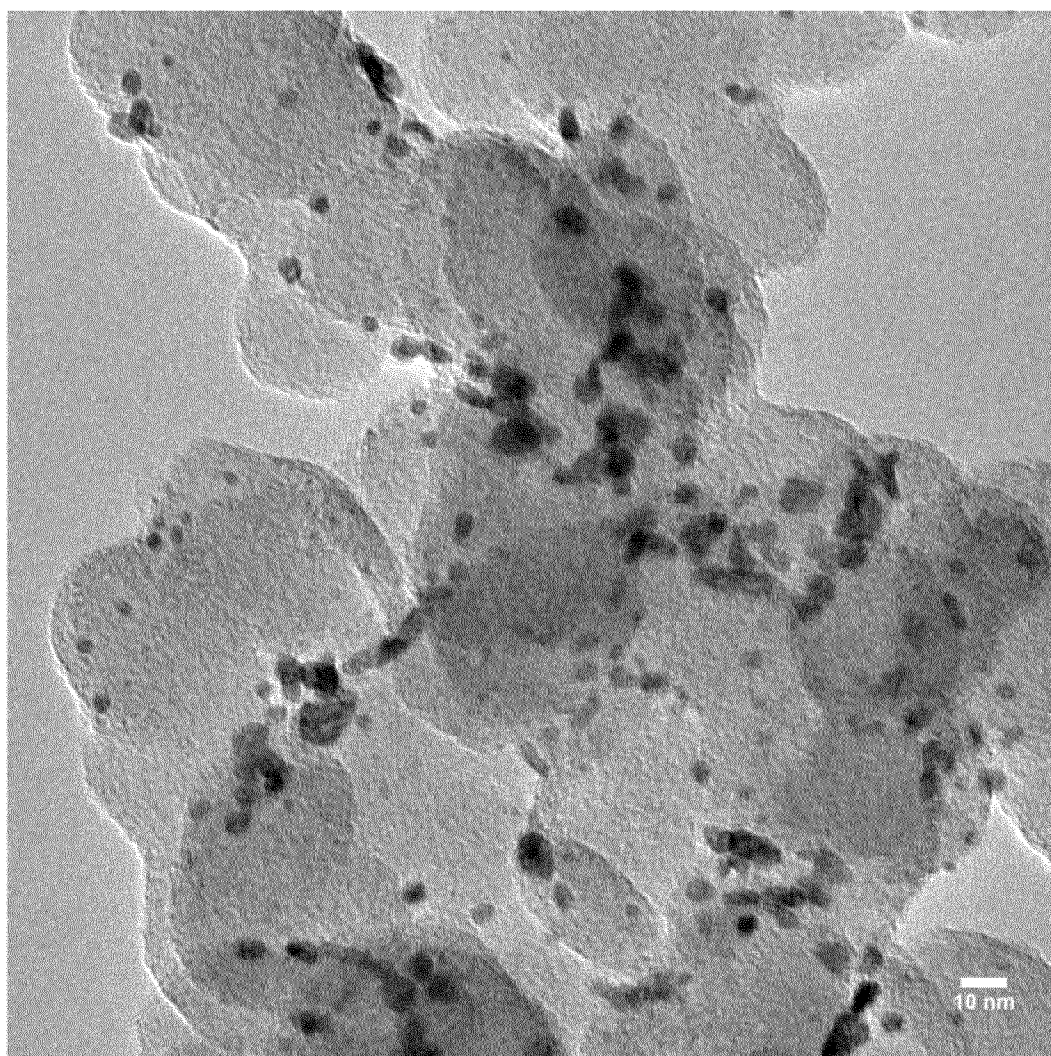
13. The process according to any one of the preceding claims, wherein steps b)
30 and c) are performed in one-pot.

14. The process according to any one of the preceding claims, wherein the alloy nanoparticle is for use in a proton exchange membrane fuel cell (PEMFC), or an electrolyzer cell.

35

15. Use of an alkali metal vapour or alkaline earth metal vapour in the production of alloy nanoparticles for the reduction of a salt of at least one alloying metal in an alloying premixture, said alloying premixture also comprising a platinum group metal.

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TEM image

Fig. 1

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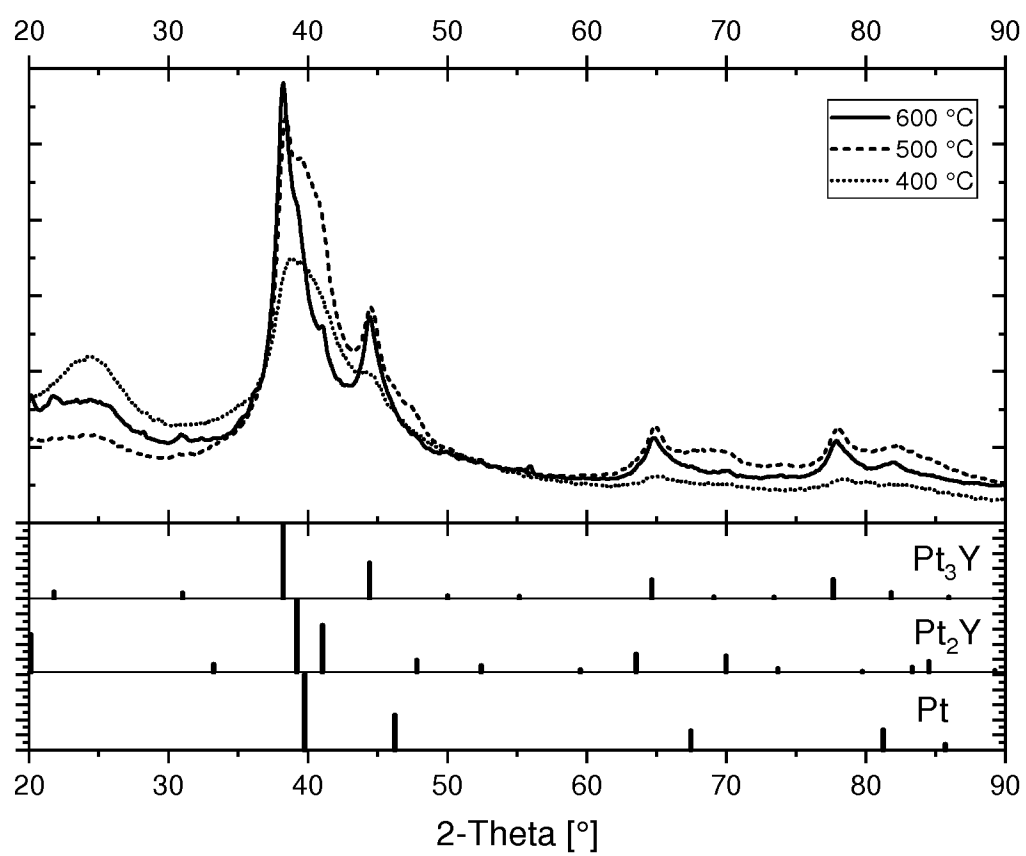


Fig. 2

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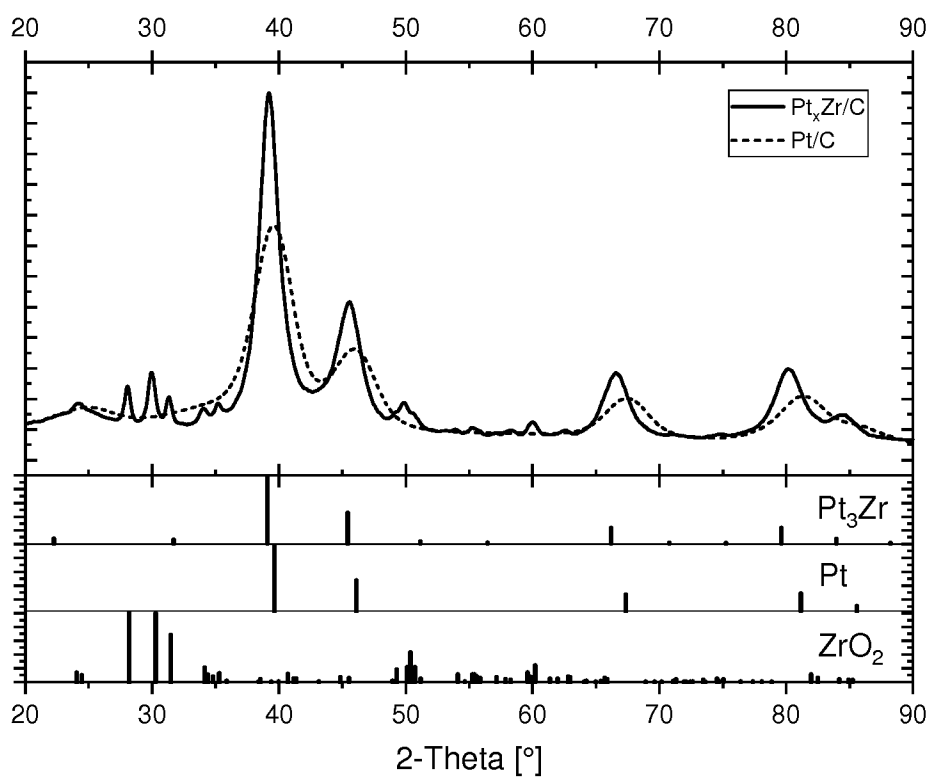


Fig. 3

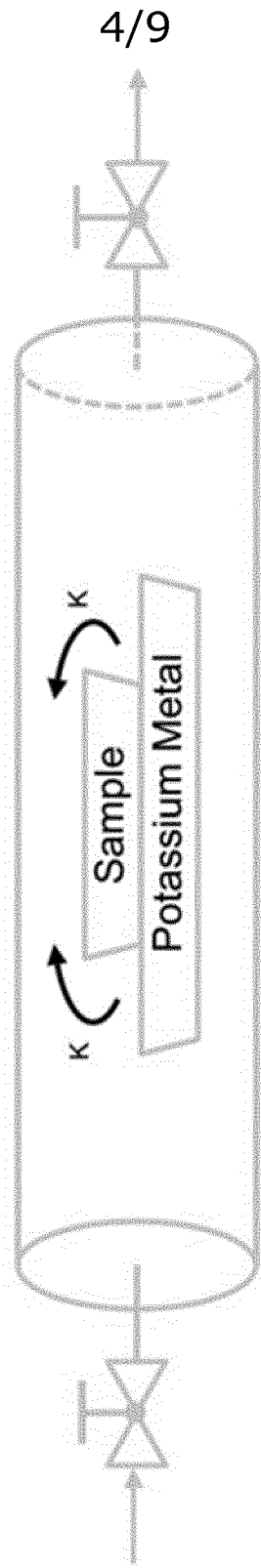


Fig. 4

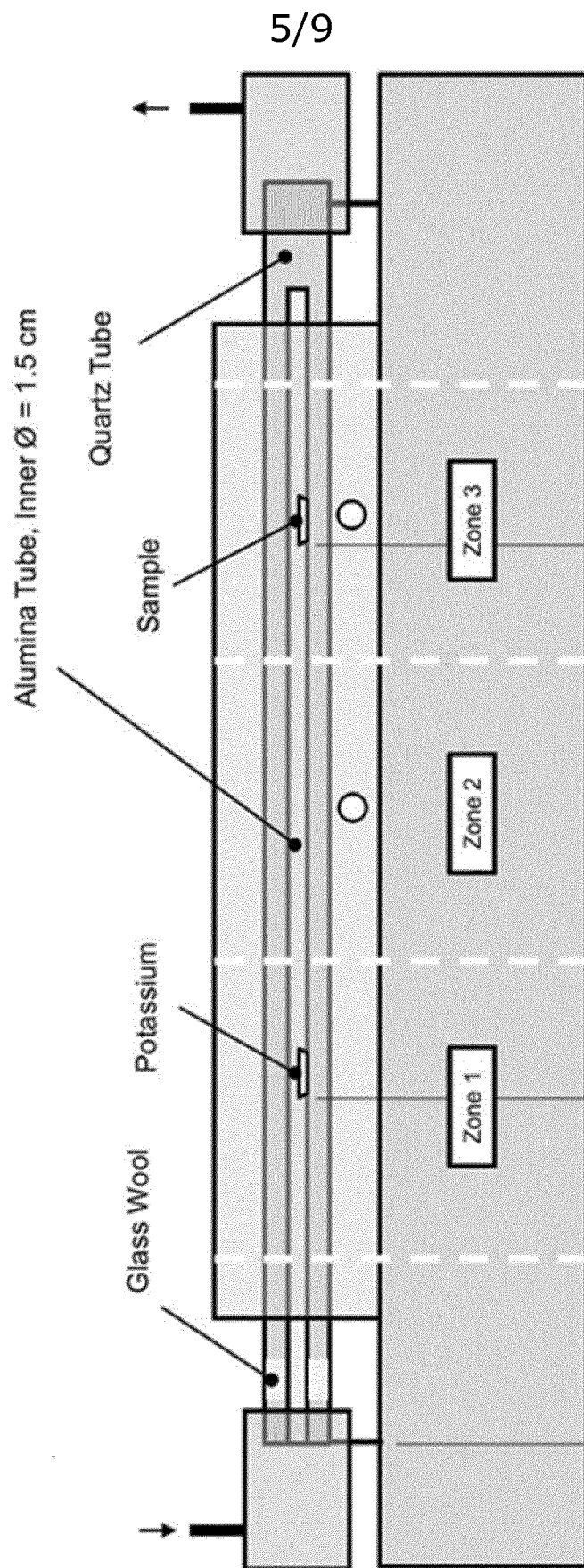


Fig. 5

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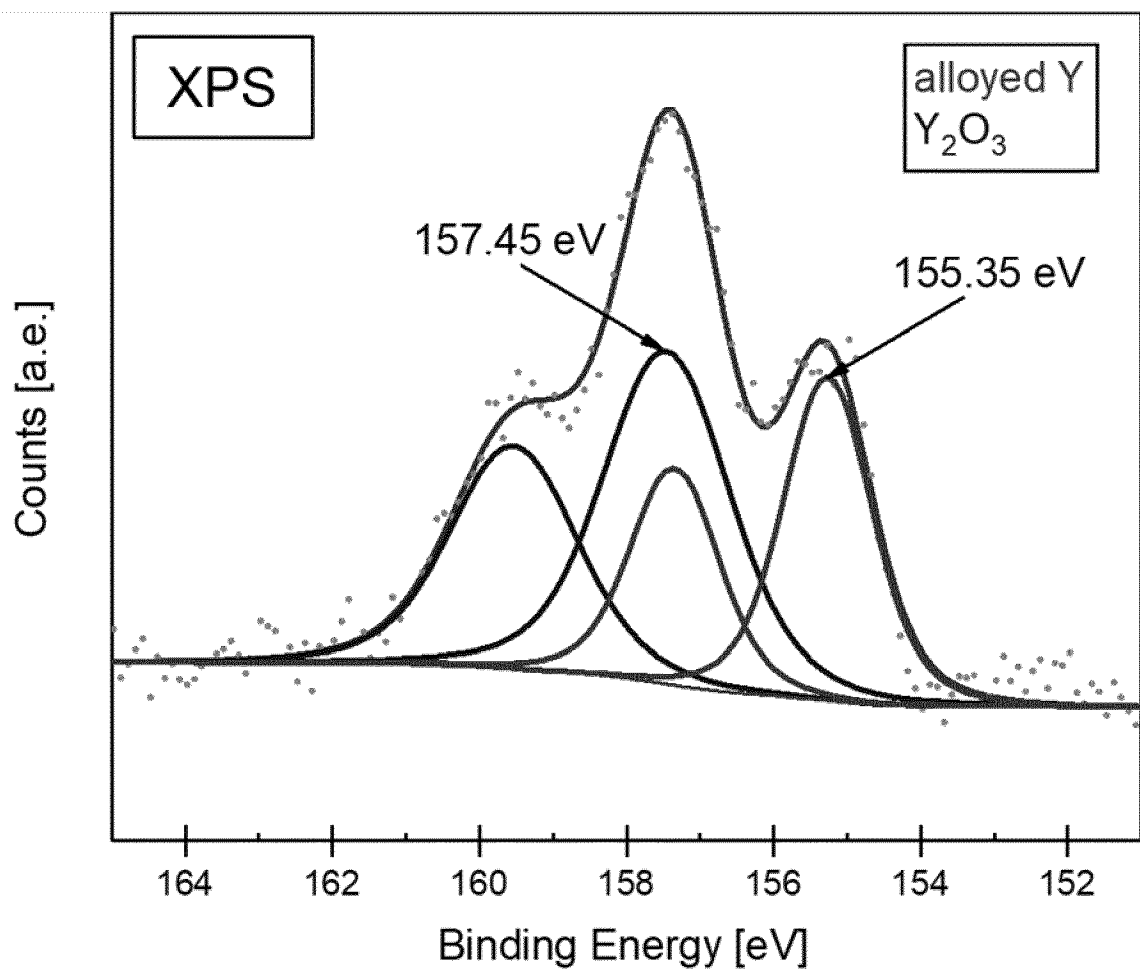


Fig. 6

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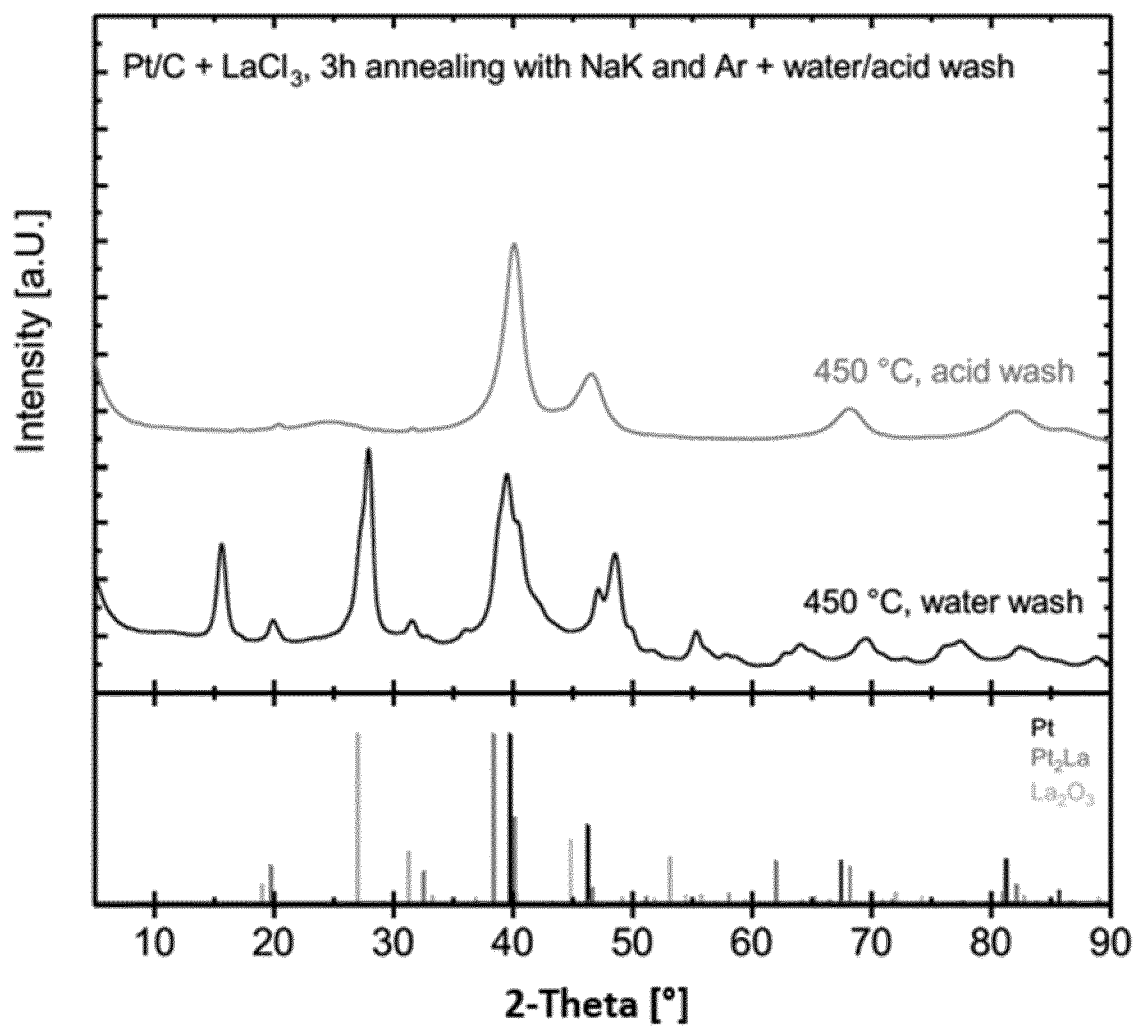


Fig. 7

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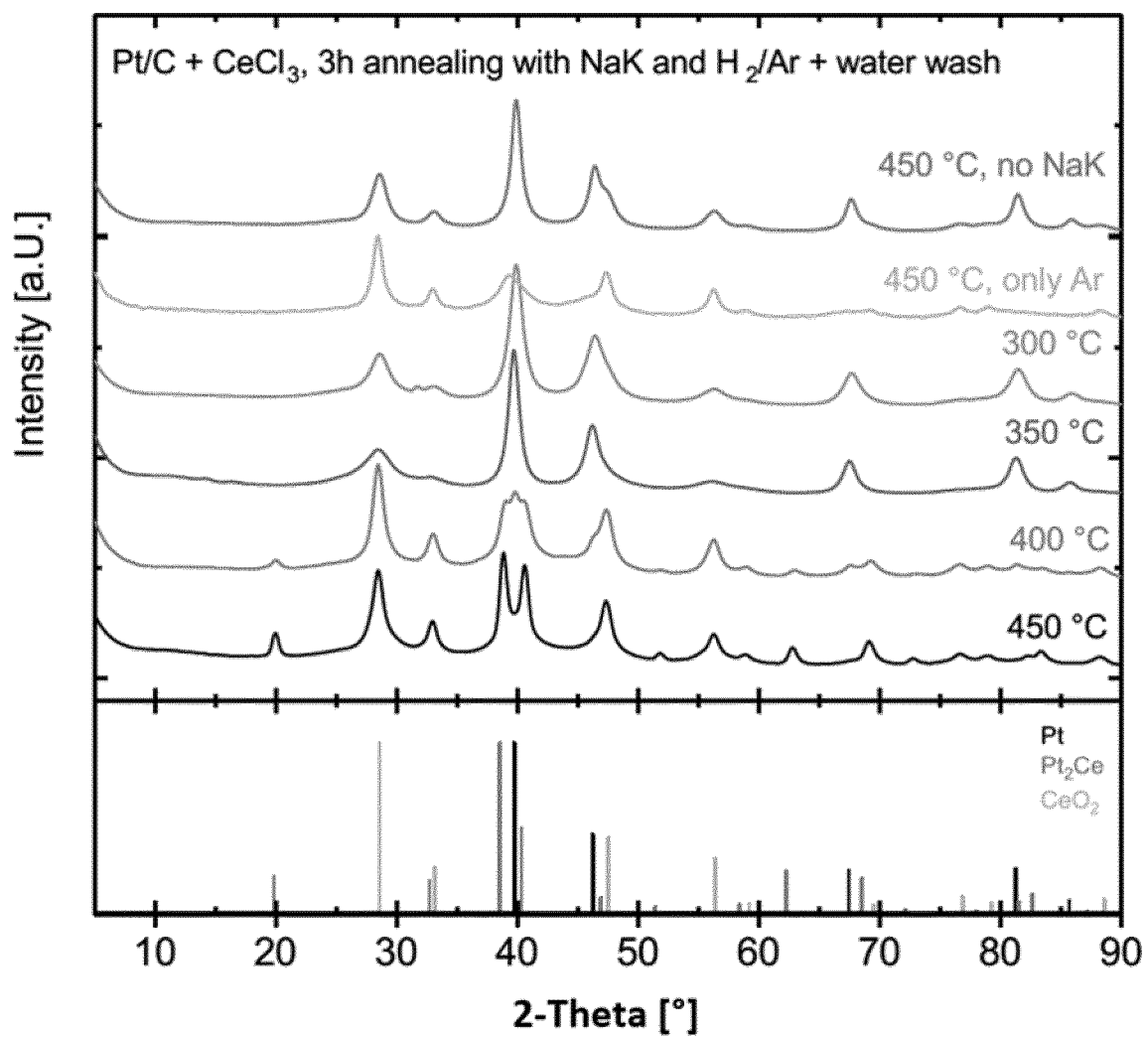


Fig. 8

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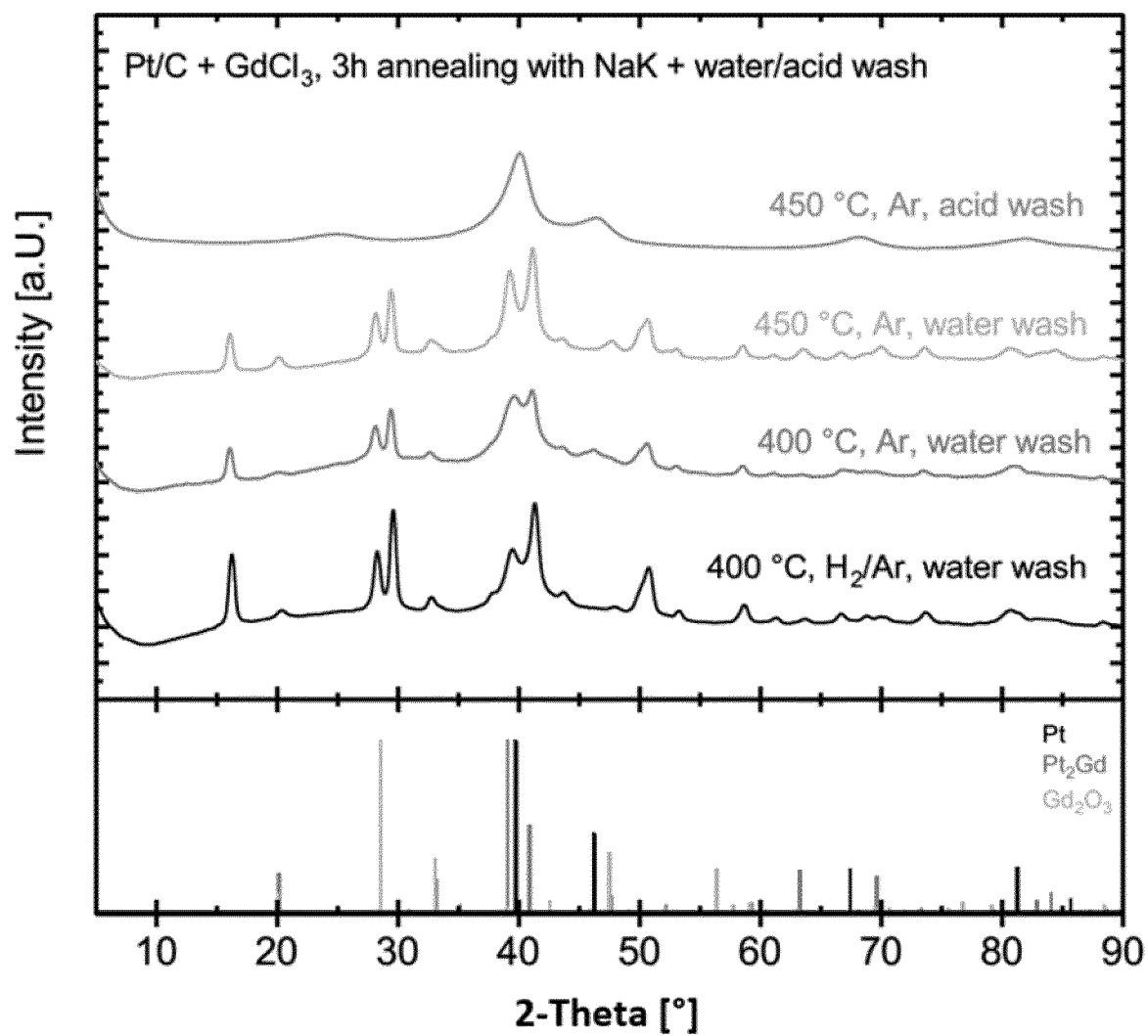


Fig. 9

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/076283

A. CLASSIFICATION OF SUBJECT MATTER INV. B01J37/08 B01J37/16 B01J35/00 B01J37/00 B01J23/42 B01J23/63 H01M8/00 B82Y30/00 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 B82Y 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 <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>Y</td> <td> WO 2017/191126 A1 (UNIV DANMARKS TEKNISKE [DK]) 9 November 2017 (2017-11-09) cited in the application abstract page 2, lines 5-28 page 6, lines 16-24 examples 1-6 ----- </td> <td>1-15</td> </tr> <tr> <td>Y</td> <td> US 4 812 301 A (DAVIDSON CHARLES F [US] ET AL) 14 March 1989 (1989-03-14) cited in the application abstract column 4, lines 12-18 examples 1-4 ----- </td> <td>1-15</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	Y	WO 2017/191126 A1 (UNIV DANMARKS TEKNISKE [DK]) 9 November 2017 (2017-11-09) cited in the application abstract page 2, lines 5-28 page 6, lines 16-24 examples 1-6 -----	1-15	Y	US 4 812 301 A (DAVIDSON CHARLES F [US] ET AL) 14 March 1989 (1989-03-14) cited in the application abstract column 4, lines 12-18 examples 1-4 -----	1-15
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.									
Y	WO 2017/191126 A1 (UNIV DANMARKS TEKNISKE [DK]) 9 November 2017 (2017-11-09) cited in the application abstract page 2, lines 5-28 page 6, lines 16-24 examples 1-6 -----	1-15									
Y	US 4 812 301 A (DAVIDSON CHARLES F [US] ET AL) 14 March 1989 (1989-03-14) cited in the application abstract column 4, lines 12-18 examples 1-4 -----	1-15									
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Date of the actual completion of the international search 3 December 2019		Date of mailing of the international search report 19/12/2019									
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Fischbach, Malaika									

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/076283

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2017191126	A1	09-11-2017	NONE

US 4812301	A	14-03-1989	NONE
