



(51) International Patent Classification:

B22F 1/00 (2006.01) B22F 9/26 (2006.01)

B22F 9/20 (2006.01) C22C 1/04 (2006.01)

B22F 9/22 (2006.01) B01J 23/63 (2006.01)

B22F 9/24 (2006.01) B01J 23/66 (2006.01)

(21) International Application Number:

PCT/EP2017/060402

(22) International Filing Date:

02 May 2017 (02.05.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

16168450.1 04 May 2016 (04.05.2016) EP

(71) Applicant: DANMARKS TEKNISKE UNIVERSITET

[DK/DK]; Anker Engelunds Vej 101 A, 2800 Kgs. Lyngby (DK).

(72) Inventors: CHORKENDORFF, Ib; Ferskengangen 20,

3460 Birkerød (DK). STEPHENS, Ifan Erfyl Lester; Linnegade 31, 1., 1361 Copenhagen K (DK). KNUDSEN,

Brian Peter; Søborg Hovedgade 63, 2. tv., 2860 Søborg (DK). VELAZQUEZ-PALENZUELA, Amado Andres; P.G. Ramms Allé 15, 2. th., 2000 Frederiksberg (DK). PEDERSEN, Christoffer Mølleskov; Jægersborgvej 68 3. th., 2800 Kgs. Lyngby (DK).

(74) Agent: PLOUGMANN VINGTOFT A/S; Rued Langgaards Vej 8, 2300 Copenhagen S (DK).

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

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ,

(54) Title: PROCESS FOR THE PREPARATION OF ALLOY NANOPARTICLES COMPRISING A NOBLE AND A NON-NOBLE METAL

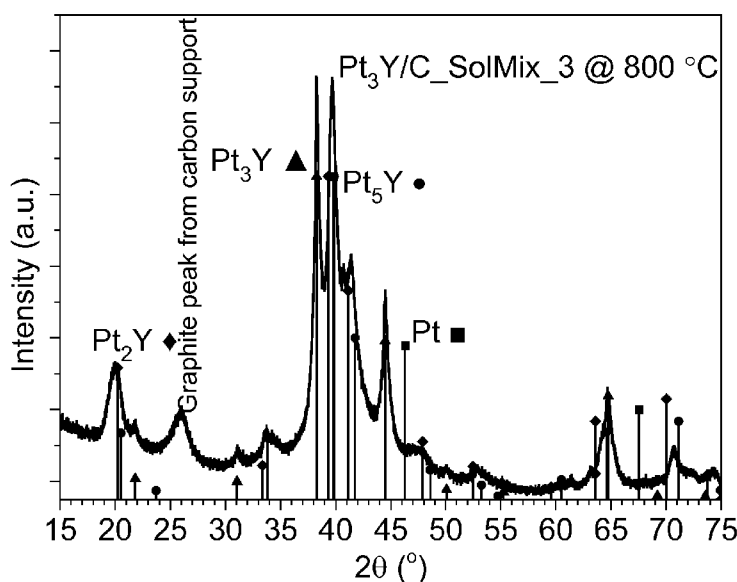


Fig. 8

(57) Abstract: The present invention concerns a chemical process for preparing nanoparticles of an alloy comprising both a noble metal, such as platinum, and a non-noble transition or lanthanide metal, such as yttrium, gadolinium or terbium. The process is carried out by reduction with hydrogen and removal of volatile species in gas form at the reaction temperature.



UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

Published:

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

PROCESS FOR THE PREPARATION OF ALLOY NANOPARTICLES COMPRISING A NOBLE AND A NON-NOBLE METAL

Field of the invention

The present invention concerns a chemical process for preparing nanoparticles of
5 an alloy comprising both a noble metal, such as platinum, and a non-noble
transition or lanthanide metal, such as yttrium, gadolinium or terbium, by
reduction.

Background of the invention

Fuel cell electrodes comprising alloys of a noble metal, such as platinum, and
10 further, non-noble metals, such as yttrium or gadolinium, are known to provide a
higher specific activity in the oxygen reduction reaction (ORR) than pure platinum
and to be quite stable under fuel cell operating conditions (WO 2011/006511, WO
2014/005599). The activities are, however, measured on bulk polycrystalline
samples. In order to function in a real fuel cell, these alloys need to be present as
15 nanoparticles.

Physical methods for preparing nanoparticles of these alloys, such as the gas
aggregation technique (Hernandez-Fernandez *et al.*, Nature Chemistry, vol. 6,
2014, 732-738), are available. However, such methods are very costly and
20 provide only small amounts of nanoparticles.

So far, the attempts of chemically synthesizing nanoparticles of alloys comprising
noble metals, such as platinum, palladium or gold and non-noble metals, such as
yttrium or gadolinium, have been unsuccessful. Various attempts have been made
25 to synthesize catalysts for ORR, but each time the outcome was that the non-
noble metal remained in oxidized form and that the resulting material therefore
was not an actual alloy (Luo *et al.*, ChemPhysChem, vol. 15, 2014, 2136-44; Liu
et al., Appl. Cat. B: Environmental, vol. 162, 2015, 593-601).

30 There is therefore a need in the art for providing a process for preparing alloy
nanoparticles comprising a noble metal and a non-noble metal. There is
furthermore a need in the art for providing such a process capable of preparing

larger amounts of particles than possible in the prior art processes and at a lower cost. The inventors of the present invention have surprisingly demonstrated to have found such a method.

5 Summary of the invention

In one aspect, the present invention concerns a process for preparing nanoparticles of an alloy comprising a noble metal and a non-noble metal, said process comprising the step of reacting a noble metal precursor and a non-noble metal precursor at a temperature in the range 300 to 1200 °C in the presence of
10 a hydrogen source, wherein the reaction is subjected to a gas flow for removing volatile species;
wherein said noble metal is selected from the group consisting of platinum, palladium, gold, and mixtures thereof, and said non-noble metal is selected from the group consisting of scandium, yttrium, lanthanum, cerium, praseodymium,
15 neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, and mixtures thereof;
wherein said noble metal precursor comprises said noble metal in metallic form or a salt containing said noble metal in oxidized form;
wherein said non-noble metal precursor comprises a salt containing said non-
20 noble metal in oxidized form;
wherein the one or more counterion(s) of said salt containing said noble metal in oxidized form and of said salt containing said non-noble metal in oxidized form form(s) a volatile species upon reaction with hydrogen, said volatile species being in gas form at the reaction temperature;
25 wherein said hydrogen source comprises hydrogen gas (H₂) and/or a species that releases hydrogen gas at the reaction temperature; and
wherein the gas in said gas flow comprises hydrogen gas, an inert gas, or a mixture thereof.

30 Brief description of the figures

Figure 1 shows the XRD spectrum of the synthesis with YCl₃ and Y(Cp)₃ as well as the Pt black precursor and the spectrum of Pt₃Y. The peak position of the most pronounced peaks are also shown for Pt (ICSD: 64923) and Pt₃Y (ICSD: 649857).

The Pt peaks are only visible in the Pt black spectrum whereas Pt₃Y peaks are visible in the three other spectra.

Figure 2 Shows detailed XPS scan of the Pt4f peak a) and Y3d peak b) of the synthesis using tris(cyclopentadienyl)yttrium(III) (Y(Cp)₃) and the Pt4f peak c) and Y3d peak b) of the synthesis using YCl₃. In a) the Pt4f peak has been fitted with two doublets where the A doublet (grey) fits metallic Pt and the B doublet (red) is another chemical state. In b) the Y3d peak was fitted using three doublets to achieve a good fit. Doublet Y3d A is attributed to metallic Y; doublet Y3d B is likely an oxide; and doublet Y3d C is attributed to yttrium carbide. In c) the Pt4f peak is broader compared to a) and is described by three doublets where one shifted up in binding energy (B red) and one is shifted down in binding energy (C blue) compared to metallic Pt (A grey). In d) the Y3d peak is convoluted with what are likely Si2s peaks. The Y3d part of the peak can be described by two doublets where one is metallic Y (Y3d A green) and the other (Y3d B purple) could be an yttrium chloride.

Figure 3 shows PXRD measurements of synthesized Pt_xY/C nanoparticles prepared using Pt/C and Y(Cp)₃ at different temperatures where a) shows the as prepared particles and b) after acid wash in 1M H₂SO₄. The points in the top mark the reference peak position of Pt (black square), Pt₃Y (blue circle) and Pt₂Y (green triangle). A and F mark the (022) Pt reflection on the as prepared and acid washed samples respectively. The peak intensity decreases with temperature, but is visible up to 900 °C. B, C, G and H mark Pt₃Y peak positions, which are visible from 550 °C and up. D and I mark the position of Pt (111), Pt₅Y (113) and Pt₂Y (113) peak position. E and J show the position of the major peak for the Y₁₈Pt_{50.56}Si_{15.44} phase.

Figure 4 Shows PXRD on samples syntheses with Pt/C and YCl₃ at different temperatures. The as prepared samples are shown in a), and b) is after acid wash in 1 M H₂SO₄. Reference peak positions for Pt (black square), Pt₃Y (blue circle), Pt₂Y (green triangle), PtSi (purple diamond), Y₂Cl₆O₁₂ (dark cyan hexagon) and YOCl (pink stars) are shown in the top. Only reference peak positions with relative peak intensity larger than 10% are shown. A, B and C mark the position of the main peaks of the Y₂Cl₆O₁₂, PtSi and YOCl phases respectively. The relative

intensities change with temperature, where $\text{Y}_2\text{Cl}_6\text{O}_{12}$ becomes stronger than YOCl at higher temperatures and PtSi becomes clearly visible at 900 °C. D shows the main Pt_3Y peak visible at 800 °C after acid wash. However, Pt peaks are still visible which can be most easily seen from peak E. At 900 °C after acid wash b) the PtSi phase F is much more intense than the Pt and Pt_xY phases G.

Figure 5 shows the $\text{Y}3d$ peak measured by XPS for the lowest temperature synthesis for; a) $\text{Y}(\text{Cp})_3$, and b) YCl_3 . The peaks have been shifted in energy so that the $\text{Pt}4f$ peaks are aligned on 71 eV for both measurements. What is clear from both samples is the presence of metallic yttrium. For the $\text{Y}(\text{Cp})_3$ catalyst, it is also seen how metallic yttrium has a component even lower than that seen for YCl_3 . For $\text{Y}(\text{Cp})_3$ the species at 158.3 eV is ascribed to the carbide, where it for YCl_3 is ascribed to unreacted precursor.

Figure 6 shows powder XRD pattern for synthesised $\text{Pt}_x\text{Y}/\text{C}$ nanoparticles using the dry mixed method. Reference lines for Pt, Pt_5Y , Pt_3Y , Pt_2Y and Pt_3Fe are shown. Reflections from Pt are not present while reflection from Pt_3Y , Pt_3Fe and other reflection close to those seen for Pt_5Y and Pt_2Y . Pt_3Fe stems from an iron contamination from the steel reactor.

20

Figure 7 shows the powder XRD of $\text{Pt}_x\text{Y}/\text{C_SolMix_2}$ with reference lines for Pt, $\text{Pt}_5\text{Y}(\text{cubic})$, Pt_3Y and Pt_2Y . While pure Pt still is present, clear reflections from the Pt_3Y phase show alloying via solvent mixing with THF.

Figure 8 shows the powder XRD of $\text{Pt}_x\text{Y}/\text{C_SolMix_3}$ with reference lines for Pt, Pt_5Y , Pt_3Y and Pt_2Y . The Pt_3Y are clearly present and in addition, one or both of the cubic Pt_2Y and Pt_5Y phases are present. The clear absence of reflections related to pure Pt is substantial evidence of complete alloying.

Figure 9 shows the powder XRD of $\text{Pt}_x\text{Y}/\text{C_SolMix_4}$ and $\text{Pt}_x\text{Y}/\text{C_SolMix_5}$ with reference lines for Pt, Pt_5Y , Pt_3Y and Pt_2Y . It is clear that the reflections from pure Pt are absent, while there are clear reflections from Pt_3Y . This is considered irrefutable evidence of alloying.

Figure 10 shows the powder XRD pattern for dry mixed $\text{Pt}_x\text{Gd}/\text{C}_3$. Included are references for Pt, Pt_5Gd and Pt_2Gd . The reflections of pure platinum are missing, but reflections from the Pt_2Gd phase appear to be present.

5 Figure 11 shows the powder XRD pattern of the $\text{Pt}_x\text{Gd}/\text{C}$ sample from solvent mixing. Reflections close to that of pure platinum are observed. However, they are shifted which could indicate a different lattice constant and therefore the presence of a Pt_xGd solid solution. The other peaks coincide with reflections from the Pt_2Gd structures.

10

Figure 12. Cyclic voltammogram of $\text{Pt}_x\text{Y}/\text{C}_{\text{SolMix}_3}$ catalyst in N_2 -saturated 0.1 M HClO_4 recorded at 50 mV s^{-1} . The first and the stable (cycle 162) potential scans are shown. The increase of the current related to H^* and $^*\text{OH}$ adsorption/desorption (at 0,05-0,04 V and 0,07-1,00 V, respectively)

15 demonstrates the cleaning of the nanoparticles.

Figure 13. CO stripping voltammogram of $\text{Pt}_x\text{Y}/\text{C}_{\text{SolMix}_3}$ catalyst in Ar-saturated 0.1 M HClO_4 recorded at 10 mV s^{-1} . First CO was adsorbed at 0.05 V vs. RHE for 2 min and then Ar was flowed through the electrolyte for 15 min to
20 remove CO in solution. The area below the peak located at $\sim 0.75 \text{ V}$ vs. RHE corresponds to the charge related to the electro-oxidation of CO adsorbed on the nanoparticles surface. By assuming a ratio of $420 \mu\text{C cm}^{-2}$ the real electrocatalyst area is estimated.

25 Figure 14. Anodic scan of $\text{Pt}_x\text{Y}/\text{C}_{\text{SolMix}_3}$ catalyst in O_2 -saturated 0.1 M HClO_4 (black) and in N_2 -saturated 0.1 M HClO_4 (background CV, red). The resulting background-corrected ORR polarization plot (blue) is also shown. Measurements performed at 50 mV s^{-1} and 1600 rpm. A well-defined mass transport limited current, I_L , is achieved at potential between 0,25 and 0,70 V vs. RHE (the value is
30 taken at 0,4 V for the calculation of the ORR kinetic current).

Figure 15. Mass-transport corrected Tafel plot (kinetic current density, j_k , versus potential, U) for the $\text{Pt}_x\text{Y}/\text{C}$ catalyst ($\text{Pt}_x\text{Y}/\text{C}_{\text{SolMix}_3}$) and pure Pt/C catalysts heat-treated at 900°C as reference. ORR activity evaluated in O_2 -saturated 0.1 M
35 HClO_4 at 50 mV s^{-1} and 1600 rpm and corrected by ohmic losses and background

current. j_k is calculated as $j_k = j^*j_L/(j_L - j)$. By convention, the catalyst activity is benchmarked at 0.9 V vs. RHE, as shown in the plot.

Figure 16. ORR mass activity (kinetic current normalized by Pt loading) for untreated Pt/C, heat-treated at 900°C Pt/C and Pt_xY/C synthesized at 800°C (Pt_xY/C_SolMix_3). An enhancement of ~60% in mass activity is achieved with the alloy nanocatalyst.

Detailed description of the invention

10 Noble metals

The noble metal of the noble metal precursor may be selected from the group consisting of platinum, palladium, gold, and mixtures thereof. In one embodiment, the noble metal is selected from the group consisting of platinum, palladium, and mixtures thereof. In a further embodiment, the noble metal is platinum.

15

Non-noble metals

The non-noble metal of the non-noble metal precursor may be selected from the group consisting of scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, and mixtures thereof. These metals are all characterized by having one or more oxidized states that are highly thermodynamically favored over the reduced, metallic form. This would explain the unsuccessful attempts so far of preparing alloy nanoparticles in metallic form including these metals.

25

Without being bound by a particular theory, the present inventors have found that the reduction reaction reducing these non-noble metals from their oxidized precursor states may be pushed towards the reduced product by adjusting the reaction conditions, in particular by removing volatile species that would otherwise cause the reverse reaction.

30

In one embodiment, said non-noble metal is selected from the group consisting of yttrium, gadolinium, terbium, dysprosium, lanthanum, samarium, cerium, and

mixtures thereof. In a further embodiment, said non-noble metal is selected from the group consisting of yttrium, gadolinium, terbium, dysprosium, samarium, and mixtures thereof. In yet a further embodiment, said non-noble metal is selected from the group consisting of yttrium, gadolinium, terbium, and mixtures thereof.

5

Precursors

The noble and non-noble metal precursors contain said noble and non-noble metals at one or more oxidation levels. The noble metal precursor may both have oxidation level 0 and/or a positive oxidation level. The non-noble metal precursor

10 has a positive oxidation level.

The counterion in the noble and non-noble metal precursors having positive oxidation levels forms a volatile species upon reaction with hydrogen, said volatile species being in gas form at the reaction temperature. In one embodiment, said

15 one or more counterion(s) are independently selected from halides, organic ligands, said organic ligands selected from the group consisting of N,N'-di-isopropylformadinato, N,N-bis(trimethylsilyl)amide, methylcyclopentadienyl, cyclopentadienyl, butylcyclopentadienyl, n-propylcyclopentadienyl, ethylenediamine, 1,5-cyclooctadiene, benzonitrile, pyridine,

20 tetramethylcyclopentadienyl, 1,2-diaminocyclohexane, 2,5-Norbornadiene, acetonitrile, 1,4,7-trimethyl-1,4,7-triazacyclononane, methyl, pentamethylcyclopentadienyl, phenyl, 2,4-dimethylpentadienyl, cycloheptene, neomenthylcyclopentadienyl, 1,3-bis(trimethylsilyl)Cyclopentadienide, 2,3-dimethylquinoxaline, phenazine,, methylborabenzene, cyclooctatetraenyl;

25 inorganic acid residues, and mixtures thereof.

In a further embodiment, said one or more counterion(s) are halides. In still a further embodiment, said halide is selected from the group consisting of chloride, bromide, iodide, and mixtures thereof. In yet a further embodiment, said halide is

30 chloride.

In another embodiment, said one or more counterion(s) are organic ligands. In still another embodiment, said organic ligands are selected from the group consisting of N,N'-di-isopropylformadinato, N,N-bis(trimethylsilyl)amide,

methylcyclopentadienyl, cyclopentadienyl, butylcyclopentadienyl, n-propylcyclopentadienyl, ethylenediamine, 1,5-cyclooctadiene, benzonitrile, pyridine, tetramethylcyclopentadienyl, 1,2-diaminocyclohexane, 2,5-Norbornadiene, acetonitrile, and mixtures thereof.

5

In a further embodiment, said one or more counterion(s) are inorganic acid residues. In yet a further embodiment, said inorganic acid residues are selected from the group consisting of hydride, nitrate, nitrite, carbonate, hydrogen carbonate, phosphate, hydrogen phosphate, dihydrogen phosphate, sulfate, hydrogen sulfate, perchlorate, chlorate, chlorite, hypochlorite, and mixtures thereof. In still a further embodiment, said inorganic acid residues are selected from the group consisting of nitrate, carbonate, hydrogen carbonate, phosphate, hydrogen phosphate, dihydrogen phosphate, sulfate, hydrogen sulfate, and mixtures thereof. In yet another embodiment, said inorganic acid residues are selected from the group consisting of nitrate, carbonate, hydrogen carbonate, and mixtures thereof.

In still another embodiment, said one or more counterion(s) are halides and/or organic ligands selected from the group consisting of N,N'-di-isopropylformadinato, N,N-bis(trimethylsilyl)amide, methylcyclopentadienyl, cyclopentadienyl, butylcyclopentadienyl, n-propylcyclopentadienyl, ethylenediamine, 1,5-cyclooctadiene, benzonitrile, pyridine, tetramethylcyclopentadienyl, 1,2-diaminocyclohexane, 2,5-Norbornadiene, acetonitrile, and mixtures thereof. In yet another embodiment, said one or more counterion(s) are halides selected from the group consisting of chloride, bromide, iodide, and mixtures thereof and/or organic ligands selected from the group consisting of N,N'-di-isopropylformadinato, N,N-bis(trimethylsilyl)amide, methylcyclopentadienyl, cyclopentadienyl, butylcyclopentadienyl, n-propylcyclopentadienyl, ethylenediamine, 1,5-cyclooctadiene, benzonitrile, pyridine, tetramethylcyclopentadienyl, 1,2-diaminocyclohexane, 2,5-Norbornadiene, acetonitrile, and mixtures thereof. In an additional embodiment, said one or more counterion(s) is chloride and/or organic ligands selected from the group consisting of N,N'-di-isopropylformadinato, N,N-bis(trimethylsilyl)amide, methylcyclopentadienyl, cyclopentadienyl, butylcyclopentadienyl, n-propylcyclopentadienyl, ethylenediamine, 1,5-cyclooctadiene, benzonitrile,

pyridine, tetramethylcyclopentadienyl, 1,2-diaminocyclohexane, 2,5-Norbornadiene, acetonitrile, and mixtures thereof.

Alloys

- 5 An alloy may be formed between two or more metal elements or between a metal and a non-metal element. In one embodiment, the alloy is formed between two or more metal elements.

Even though the alloys are exemplified herein as binary alloys, the alloys may
10 have more than two different components. Thus, in one embodiment, the alloy is a binary, ternary, or quaternary alloy. In a further embodiment, the alloy is a binary or ternary alloy. In still a further embodiment, the alloy is a binary alloy.

Hydrogen source

- 15 In order to carry out the reduction process of the invention, a source of hydrogen is needed. The hydrogen source may be hydrogen gas (H_2) or a compound that releases hydrogen gas at the reaction conditions of the process of the invention. Such compounds may be sodium borohydride, lithium borohydride, aluminum borohydride, ammonia, methane, ethane, propane, butane, pentane, *n*-hexane,
20 cyclohexane, or hydrazine.

Thus, in one embodiment, the hydrogen source is selected from the group consisting of be hydrogen gas (H_2), sodium borohydride, lithium borohydride, aluminum borohydride, ammonia, methane, ethane, propane, butane, pentane, *n*-
25 hexane, cyclohexane, and hydrazine. In a further embodiment, said hydrogen source is hydrogen gas.

Gas flow

- The process of the invention involves a gas flow, which serves to remove volatile
30 species from the reaction chamber. Hydrogen gas may serve a double purpose in being both a hydrogen source for the reaction while at the same time removing volatile species resulting from the reaction. Hence, in one embodiment, the gas flow comprises hydrogen gas.

The gas used for the gas flow may also be a gas that is inert under the reaction conditions of the process of the invention. Accordingly, in one embodiment of the invention, the gas in the gas flow comprises helium, neon, argon, krypton, xenon, nitrogen, or a mixture thereof. In another embodiment, the gas in the gas flow
5 comprises helium, neon, argon, krypton, xenon, nitrogen, or a mixture thereof together with hydrogen gas.

The flow rate of the gas flow is selected based on the reactor, the precursor and the amount thereof, the reaction time, and the reaction pressure among other
10 factors. Thus, a gas flow rate of 1 to 10000 ml/min may be used in the process of the invention. In one embodiment, the gas flow rate is in the range of 10 to 1000 ml/min. In a further embodiment, the gas flow rate is in the range of 20 to 800 ml/min. In still a further embodiment, the gas flow rate is in the range of 40 to 500 ml/min. In yet a further embodiment, the gas flow rate is in the range 50 to
15 300 ml/min.

Temperature

The present inventors have found that a high temperature is needed to accomplish reduction of the non-noble metal. Thus, the process of the invention is
20 carried out at a temperature in the range 300 to 1200 °C. In one embodiment, the temperature is in the range 400 to 1100 °C. In a further embodiment, the temperature is in the range 500 to 900 °C, such as in the range 550 to 800 °C.

Nanoparticles

25 The aim of the process according to the invention is to prepare particles on the nanoscale for use in a fuel cell. Thus, in one embodiment, the D₅₀ particle diameter of the nanoparticles prepared in the process according to the invention is in the range 2 to 20 nm. In a further embodiment, the D₅₀ particle diameter is in the range 3 to 15 nm. In yet a further embodiment, the D₅₀ particle diameter is in
30 the range 6 to 12 nm. By the term "D₅₀ diameter" is understood that 50% of the particles have a diameter of less than the D₅₀ diameter. The particle size distribution of the particles may e.g. be measured using a Helos® Sympatec GmbH laser diffraction apparatus.

Examples

Example 1: Preliminary drying of Pt/C used as precursor

Approximately 1 g of carbon-supported Pt nanoparticles catalyst (Tanaka Kikinzoku Kogyo (TKK), 50 wt.% Pt loading and ~6,6 nm crystal size according to X-ray diffraction (XRD)) was loaded in a cylindrical carbon crucible made from a rolled graphite foil (Alfa Aesar, 99.8%; 0.254 mm thickness), introduced in a custom-made steel reactor and sealed using CF flanges and copper gaskets. Following this, the reactor was placed in the tube furnace and connected to gas lines via VCR fittings with copper gaskets (inlet: inert/ reagent gas; outlet: exhaust with 1/8" coil of 3 meters open to air).

High-purity hydrogen (AGA N6, scientific purity (99.9999%)) was circulated through the system with a flow of 100 ml/min for at least 20 minutes before start of the heating procedure in order to remove the air from the reactor, or to replace the argon trapped in the reactor when the mounting is performed inside the Ar-filled glovebox (Vacuum Atmospheres, oxygen and water moisture below 0,5 ppm). After this time, the temperature was increased from room temperature (~23°C) up to 200°C in 30 minutes and then kept at this temperature for an additional 60 minutes, followed by unrestrained cooling down to room temperature.

Once the temperature was stable, the hydrogen flow was switched to argon (AGA N5, instrumental purity (99.999%)) with a flow of 10 ml/min and maintained for at least 30 min to purge the reactor of hydrogen. Then, the steel reactor was removed from the heating source, loaded into the Ar-filled glovebox and opened. The dried Pt/C precursor was stored in a glass vial in the glovebox for further use.

In the examples below including Pt Black (Johnson Matthey HiSPEC 100 >95% and 11 nm average particle size, according to the supplier) and the organometallic precursor Tris(cyclopentadienyl)yttrium(III) (Sigma-Aldrich, 99.9%), a quartz reactor was used. This reactor resembles the metal reactor above in function and was also handled in a glovebox prior to annealing procedures.

Instead of metal tubing and connection, simple food grade rubber tubing was used. This was connected to a Schlenk line in such a way that both inlet and outlet was evacuated and refilled three times before opening to the reactor. The outlet on the Schlenk line was connected to an oil trap. The Pt Black was dried in the same manner as the Pt/C described above by annealing to 200 °C in 30 minutes and keeping the temperature for 60 minutes. Samples prepared in the quartz reactor are denoted with a Q after their sample number.

Example 2: Synthesis of Pt_xY/C catalyst from Pt Black, Pt/C, YCl₃ and

10 Tris(cyclopentadienyl)yttrium(III) as precursors using *dry mixing* (Pt_xY/C i)

For the synthesis of ~100 mg of Pt_xY catalyst, Pt Black, dried as described in example 1, and Tris(cyclopentadienyl)yttrium(III), used without further purification, were mixed with a weight ratio for Pt:Y of 0.33, yielding an atomic mixing ratio for Pt:Y of 0.48. This was then mixed and ground in the Ar-filled glovebox using an agate mortar and pestle (Sigma-Aldrich, diameter 75mm) until uniformity of color and granularity. From here it was loaded into the quartz reactor and subjected to reduction in H₂ at 900 °C.

For samples with Tris(cyclopentadienyl)yttrium(III) in the quartz reactor, the following program was followed while flowing H₂ at 100 mL/min: 10 °C/min for 20 min then holding at this temperature for 60 min in order to reduce/decompose the precursor before the sublimation point, then 10 °C/min until 900 °C and then kept there for 60 min before being brought down to 500 °C in 20 min and left here for 30 min followed by free cool down. The samples with YCl₃ in the quartz reactor were heated with a steady ramp of 10 °C/min until 900 °C and then held here for 6 hours followed by free cooling. During the whole process a constant flow of H₂ was kept at 100 mL/min. The as-prepared catalyst located in the reactor was then moved to the glovebox and the product was recovered and taken out to pacify in air.

30

Powder X-ray Diffraction (PXRD) measurements of the synthesised samples are shown in Figure 1 and compared to the Pt black powder and a polycrystalline Pt₃Y disk. The synthesised samples do not have any of the Pt reflections, but all of the Pt₃Y reflections, which shows the formation of the alloy. Figure 2 shows X-ray

Photoelectron Spectroscopy (XPS) measurements of the Pt4f and Y3d peaks for the two synthesised samples. The measured peaks have been deconvoluted into Pt4f doublets, Y3d doublets and Si2s peaks. The Y3d_{5/2} peak observed below 156 eV in both samples is a clear evidence of metallic Yttrium. The major Pt4f_{7/2} peak is also metallic and the combined PXRD and XPS results show the formation of a metallic Pt₃Y alloy for both samples synthesised from either YCl₃ or Tris(cyclopentadienyl)yttrium(III).

- PXRD measurements of synthesised Pt_xM/C nanoparticles from Pt/C and Tris(cyclopentadienyl)yttrium(III) at different temperatures are shown in Figure 3. The reflections from the Pt₃Y phases, marked B and C, are present from 550 °C, showing at least partial alloying from 550 °C. The Pt₃Y phase is not present at 500 °C, but additional reflections besides that of Pt and graphite are present, which could indicate another Pt_xY phase. Figure 4 shows PXRD data for samples synthesised from Pt/C and YCl₃ at different temperatures. On the left side, the samples were measured as prepared and on the right side the sample were measured after being treated in 1 M H₂SO₄. The measurements of the as prepared samples are dominated by Yttrium-oxychlorides species, which can be removed by acid wash in 1 M H₂SO₄ as seen on Figure 4b. After acid treatment PtSi, Pt_xY and Pt phases are observed, which shows that at high temperatures the precursor is reacting with the quartz reactor. Pt₃Y and Pt₂Y phases are clearly seen from 800 °C and above, however, below 800 °C a shoulder is observed on the Pt peak at ~40°, which could be an alloy phase.
- Figure 5 shows the XPS measurements of the lowest temperature samples from each temperature series. These show that both samples contain metallic Yttrium, even though the PXRD does not show indisputable evidence of alloying at these temperatures. These measurements, together with the PXRD results, show that Pt_xM alloy phases can be formed from 700 °C using YCl₃ as precursor and from 500 °C using Y(Cp)₃, although the conversion is larger at higher temperatures. Table 1 summarizes the amount of Pt(/C) precursor and TrisY precursor used for preparing Pt_xY(/C) catalyst.

Table 1. Amounts of Pt(/C) and Tris(Cp)yttrium(III) (TrisY) used for the dry mixing synthesis of Pt _x Y/C				
Sample	Precursor at. ratio: Pt:Y	Mass of Pt(/C) catalyst / mg	Mass of TrisY / mg	Annealing temperature / °C
Pt _x Y_1Q	0.48	108	330	900
Pt _x Y/C_1Q	0.48	322 (Pt/C)	484	900
Pt _x Y/C_2Q	0.22	150 (Pt/C)	502	900
Pt _x Y/C_3Q	0.21	150 (Pt/C)	515	800
Pt _x Y/C_4Q	0.22	149 (Pt/C)	498	800
Pt _x Y/C_5Q	0.22	128 (Pt/C)	429	700
Pt _x Y/C_6Q	0.21	155 (Pt/C)	550	600
Pt _x Y/C_7Q	0.20	151 (Pt/C)	550	550
Pt _x Y/C_8Q	0.22	121 (Pt/C)	400	500

For the synthesis of ~200 mg of Pt_xY/C catalyst with an atomic mixing ratio, Pt:Y, of 0.1, 200 mg of dried Pt/C, obtained as described in Example 1, were mixed in the Ar-filled glovebox with 1000 mg of YCl₃ precursor (Sigma-Aldrich, anhydrous 99,99%), without further purification, using the agate mortar and pestle mentioned above. The mixture was carefully ground until a homogeneous powder was achieved and then loaded in a graphite crucible, introduced in the custom-made steel reactor and sealed. Starting from this point, the further process resembles the procedure for the catalyst drying in Example 1 except for the temperature program. In this way, the temperature was increased up to 800°C using a ramp of 40 °C/min for 10 min, then 10 °C/min for 20 min and finally 30 min was then used to reach the 800 °C, which was kept for 6 h and then followed by free cooling down to room temperature. H₂ was flowing through the reactor throughout the high temperature (>100°C) phase at 100 mL/min. The as-prepared catalyst located in the reactor was then moved to the glovebox and the product was recovered and taken out to pacify in air. A PXRD measurement of the sample is shown in Figure 6. Pt₂Y, Pt₃Y and possibly Pt₅Y phases are seen while no Pt phase is observed, indicating full conversion of the Pt. In addition to the Pt_xY phases, a Pt₃Fe phase is also seen, which is likely due to a reaction with the steel reactor.

The experimental procedure detailed in this example was used to synthesize Pt_xY/C. Table 2 summarizes the amount of Pt(/C) precursor and YCl₃ salt used for preparing Pt_xY(/C) catalyst.

Table 2. Amounts of Pt(/C) and YCl ₃ used for the dry mixing synthesis of Pt _x Y/C				
Sample	Precursor ratio: at. Pt:Y	Mass of Pt(/C) catalyst / mg	Mass of YCl ₃ / mg	Annealing temperature / °C
Pt _x Y_2Q	0.25	76	310	900
Pt _x Y/C_9Q	0.33	400 (Pt/C)	606	900
Pt _x Y/C_10Q	0.14	195 (Pt/C)	682	900
Pt _x Y/C_11Q	0.1	205 (Pt/C)	1001	800
Pt _x Y/C_12Q	0.1	201 (Pt/C)	1000	700
Pt _x Y/C_13Q	0.12	232 (Pt/C)	1001	750
Pt _x Y/C_14Q	0.1	201 (Pt/C)	1011	800
Pt _x Y/C_15	0.1	200 (Pt/C)	1000	800

5

Example 3: Synthesis of Pt_xY/C catalyst from Pt/C and YCl₃ as precursors using solvent mixing (Pt_xY/C SolMix i)

For the synthesis of ~200 mg of Pt_xY/C catalyst with a Pt:Y atomic precursor pre-mixing ratio of 3 using a solvent mixing procedure, 37 mg of YCl₃ precursor (Sigma-Aldrich, anhydrous 99.99%), without further purification, were dissolved in varying volumes of tetrahydrofuran (THF) (Sigma-Aldrich, anhydrous inhibitor free, ≥99.9%) or acetonitrile (Sigma-Aldrich, anhydrous, 99.8%). The THF was further dried over metallic sodium (Sigma-Aldrich, 99.95%) with benzophenone (Sigma-Aldrich, ReagentPlus® 99%) until the characteristic deep blue/purple color of the benzophenone ketyl radical appeared[1], and then stored over a 3A molecular sieve in the glovebox. The acetonitrile was used without further drying procedures.

The dissolution was done in an in an open glass vial inside the Ar-filled glovebox. The solution was stirred using a glass-covered magnetic stirrer bar at 250 rpm over a stirring plate until the precursor was completely dissolved (usually within 1-2 min). Subsequently, 200 mg of dried Pt/C, obtained as described in Example

1, were added over the YCl_3 solution and the resulting slurry was stirred for at least 72 h in the glovebox. During this time, the solvent slowly evaporates given its volatility (vapor pressure of 90 mm Hg at 25°C) and the result is a powder that is used in the following synthesis steps as described in Example 2 for the dry catalyst/ YCl_3 mixture. To guarantee the complete elimination of solvent traces, the mixture may be heated in a hot plate at a mild temperature (40-50°C) or connected to a pump system to eliminate the solvent by vacuum distillation.

$\text{Pt}_x\text{Y/C}$ catalysts with different Pt:Y atomic ratios could be obtained using the solvent mixing route. The amounts of Pt/C catalyst and YCl_3 precursor as well as the volume of solvent used in the synthesis are shown in Table 3.

Table 3. Amounts of Pt/C, YCl_3 , and acetonitrile used in the solvent mixing synthesis of $\text{Pt}_x\text{Y/C}$					
Sample	Precursor ratio: at. Pt:Y	Volume of solvent / mL	Mass of Pt/C catalyst / mg	Mass of YCl_3 / mg	Annealing temperature / °C
$\text{Pt}_x\text{Y/C_SolMix_1}$	3	3 (THF)	201	37	800
$\text{Pt}_x\text{Y/C_SolMix_2}$	1.5	3 (THF)	80	27	800
$\text{Pt}_x\text{Y/C_SolMix_3}$	1.5	15 (acetonitrile)	202	80	800
$\text{Pt}_x\text{Y/C_SolMix_4}$	1.5	15 (acetonitrile)	202	74	800
$\text{Pt}_x\text{Y/C_SolMix_5}$	1.5	15 (acetonitrile)	202	78	800

In figures 7, 8 and 9, PXRD pattern from catalysts prepared as described in the preceding example are shown. For figure 7, where THF was used a solvent, it is seen how reflections from Pt_2Y , Pt_3Y and possibly Pt_5Y are present. At the same time, reflections from pure Pt are still evident, indicating sub-optimal mixing. In comparison, the PXRD patterns in both figures 8 and 9, where acetonitrile was used as solvent, show no reflections from pure Pt. In addition, the reflections from the Pt_3Y phase are much more prominent, indicating a higher phase-fraction than for the catalyst in figure 7.

in figure 12 through 16, electrochemical measurements of Pt_xY/C_SolMix_3 (PXRD pattern shown in figure 8) are shown. Figure 14 shows the anodic sweep of the CV in Nitrogen saturated (red line) and oxygen saturated (black line) electrolyte, as well as the CV in oxygen saturated electrolyte corrected for the capacitance seen in CV in nitrogen (blue line). This is done under the assumption that the capacitances are similar in oxygen and nitrogen saturated electrolytes. Figure 15 shows the specific activity (activity per surface area of catalyst) of the catalyst compared to that of the Pt/C used in the synthesis. The surface area is found by analysing the CO stripping feature seen in figure 13, between 0.6 and 0.8 V vs RHE. It is clear that the catalyst is more active at the per area level, and figure 16 show that this activity increase also carries over to the mass activity of the catalyst.

Example 4: Synthesis of Pt_xGd/C and Pt_xTb catalysts from Pt/C and GdCl₃/TbCl₃ as precursors using *dry mixing* (Pt_xGd/C *i*, Pt_xTb/C *i*)

The dry mixing procedure used for the preparation of Pt_xY/C catalysts described in Example 2 can be adapted for the synthesis of Pt_xGd/C and Pt_xTb/C catalysts. Such purpose only requires the replacement of the YCl₃ precursor by GdCl₃ or TbCl₃ (in both cases Sigma-Aldrich, anhydrous 99.99%) to yield Pt_xGd/C or Pt_xTb/C catalysts, respectively.

Figure 10 shows the PXRD of Pt_xGd/C prepared by dry mixing. Here the alloying gives rise to the Pt₂Gd phase and the absence of pure Pt.

Table 4 and Table 5 summarize the amounts used in the synthesis of the alloy catalysts with the specified Pt:Gd and Pt:Tb ratios, respectively.

Table 4. Amounts of Pt/C and GdCl ₃ used in the dry mixing synthesis of Pt _x Gd/C				
Sample	Precursor ratio: at. Pt:Gd	Mass of Pt/C catalyst / mg	Mass of GdCl ₃ / mg	Annealing temperature / °C
Pt _x Gd/C_1Q	0.1	200	1362	800
Pt _x Gd/C_2Q	0.1	208	1368	700
Pt _x Gd/C_3	0.1	208	1270	800

Table 5. Amounts of Pt/C and TbCl ₃ used in the dry mixing synthesis of Pt _x Tb/C				
Sample	Precursor ratio: at. Pt:Tb	Mass of Pt/C catalyst / mg	Mass of TbCl ₃ / mg	Annealing temperature / °C
Pt _x Tb/C_1Q	0.11	212	1357	800
Pt _x Tb/C_2	0.1	224	1399	800

5

Example 5: Synthesis of Pt_xGd/C and Pt_xTb catalysts from Pt/C and GdCl₃/TbCl₃ as precursors using solvent mixing (Pt_xGd/C AcCN i, Pt_xTb/C AcCN i)

The introduction of acetonitrile as solvent to favor the mixing of Pt/C and GdCl₃/TbCl₃ salts is also feasible, as described in Example 3 for Pt_xY/C, and only
 10 requires replacing the yttrium salt by GdCl₃ or TbCl₃ (in both cases Sigma-Aldrich, anhydrous 99.99%).

Similar to the dry mixing of precursors in Example 4, the Pt:lanthanide ratios in the resulting alloy catalysts could vary by choosing the appropriated amount of
 15 Pt/C, precursor salt and acetonitrile. This information is collected in Table 6 and Table 7 for Pt_xGd/C and Pt_xTb/C catalysts, respectively, with different stoichiometry.

In figure 11, Pt_xGd/C prepared by solvent mixing is analyzed by PXRD. From
 20 figure 11 it is seen that Pt is still present. However, the reflections are shifted to

higher angles indicating a change in lattice parameter for the structure. The other peaks coincide with reflections from the Pt₂Gd structures.

Table 6. Amounts of Pt/C, GdCl ₃ , and acetonitrile used in the solvent mixing synthesis of Pt _x Gd/C					
Sample	Precursor ratio: at. Pt:Gd	Volume of acetonitrile / mL	Mass of Pt/C catalyst / mg	Mass of GdCl ₃ / mg	Annealing temperature / °C
Pt _x Gd/C_SolMix_1	1.5	15	200	91	800

Table 7. Amounts of Pt/C, TbCl ₃ , and acetonitrile used in the solvent mixing synthesis of Pt _x Tb/C					
Sample	Precursor ratio: at. Pt:Tb	Volume of acetonitrile / mL	Mass of Pt/C catalyst / mg	Mass of TbCl ₃ / mg	Annealing temperature / °C
Pt _x Tb/C_SolMix_1	1.5	15	200	100	800

5

Example 6: Synthesis of Pt_xY/C catalyst using PtCl₄ and YCl₃ as precursors (Pt_xY/C salts i)

- 10 The synthesis of Pt_xY/C catalysts is also achievable using a Pt salt as precursor of the noble metal, as an alternative to carbon-supported Pt nanoparticles. In a typical synthesis aiming for a Pt:Y atomic ratio of 1.5 and a Pt loading of 40 wt.%, 108 mg of PtCl₄ (Merck, anhydrous, 57.5% Pt) and 43 mg of YCl₃ (Sigma-Aldrich, anhydrous 99.99%) were added over 13mL of acetonitrile (Sigma-Aldrich,
- 15 anhydrous, 99,8%) in an open glass vial and stirred until complete dissolution over a stirring plate at 250 rpm. Once the precursors were dissolved (within 1-2 min), 121 mg of Vulcan XC-72R carbon black (Fuel Cell store), previously dried as described in Example 1, were added to the mixture and stirred for 72 h. After slow evaporation of the solvent, the resulting powder was treated as detailed in
- 20 Example 2 and Example 3.

As in the case of Example 3, this procedure allows preparing Pt_xY/C catalysts with different Pt:Y atomic ratios by tuning the amounts of $PtCl_4$, YCl_3 and the volume of acetonitrile. Additionally, it also facilitates the design of catalysts with different metallic loading by changing the precursors:carbon ratio. Some examples of the

5 catalysts prepared using this method, are collected in Table 8.

Table 8. Amounts of $PtCl_4$, YCl_3 , acetonitrile and Vulcan XC-72 carbon used in the solvent mixing synthesis of Pt_xY/C							
Sample	Precursor ratio: at. Pt:Y	Intended metal loading / wt. %	Volume of acetonitrile / mL	Mass of $PtCl_4$ / mg	Mass of YCl_3 / mg	Mass of Vulcan XC-72 carbon / mg	Annealing temperature / °C
Pt_xY/C_salts_1	1.5	40	13	108	43	121	800
Pt_xY/C_salts_2	3	40	21	122	25	121	800

Example 7: Post-treatment of the Pt_xM/C ($M = Y, Gd, Tb$) catalysts

- 10 After the synthesis, the as-prepared Pt_xM/C alloy catalysts are exposed to air and washed in order to eliminate impurities and unreacted soluble reagents. The washing may be performed only with ultra-pure water (Millipore Milli-Q, resistivity > 18 MΩ cm, TOC < 3 ppb), but acid washing is preferred. Acid washing makes it possible to dissolve non-noble metallic oxides, otherwise insoluble in neutral
- 15 solution. Such step may be carried out with any solution acidic enough (pH < 7), but typical washing solutions are $HClO_4$ 0.1 M (from 70% $HClO_4$ Merck Suprapur) and H_2SO_4 0.5 M (from 96% H_2SO_4 Merck Suprapur). In a typical washing operation, the powder catalyst is mixed with ~20 mL of acid solution, stirred and sonicated for 15-30 min and centrifuged at 12,000 rpm. Once this is done, the
- 20 supernatant is removed and the operation is repeated at least 3 more times using ultra-pure water. Finally, the catalyst is allowed to dry on a watch-glass at room temperature or under a slightly warm air stream (40-50 °C).

The described acid washing process is also suitable for cleaning the carbon black

25 of leachable metals when being used as detailed in Example 6. This procedure

may be carried out prior to the drying in the reactor according to the procedure in Example 1.

Example 8: X-ray diffraction (XRD) characterization of the Pt_xM/C (M = Y, Gd, Tb)

5 catalysts

Water-washed or acid-washed Pt_xM/C catalysts were subjected to XRD analysis in order to confirm the formation of intermetallic compounds with a long-range ordered structure. For such purpose, the powder catalyst is loaded on a zero-background plate either dry or suspended in a volatile solvent (isopropanol, Sigma-
10 Aldrich, ACS reagent, 99.8%) and mounted in the equipment (Panalytical X'Pert Pro) in a transmission spinner stage configuration. The measurement is computer-controlled with the Panalytical X'Pert Data Collector software. The angle 2θ was varied between 15 and 90° in continuous mode and minimum 3 scans were recorded per analysis in order to increase the signal-to-noise ratio.

15

Data treatment of the collected XRD patterns was performed with the Panalytical HighScore Plus Collector software, which also provided the database with the experimental XRD patterns used as reference (additional XRD patterns for comparison purpose were taken from the online Inorganic Crystal Structure
20 Database (ICSD)-Karlsruhe and in-house measurements on polycrystalline alloy stubs from MaTeck®[2][3]).

Example 9: X-ray photoelectron spectroscopy (XPS) analysis of the Pt_xM/C (M = Y, Gd, Tb) catalysts

25 Acid-washed Pt_xM/C catalysts were characterized using XPS technique. The principle behind this technique is that by measuring the kinetic energy of the photoelectrons escaping, the sample being irradiated with a beam of X-rays, it is possible to estimate the elemental composition of a catalyst as well as the chemical state of the elements present.

30

XPS is a surface-sensitive technique and only photoelectrons from the outermost surface of the sample (< 5 nm) escape and can be detected, so the obtained composition reflects only this fraction of the sample. In this particular case, the XPS analysis allows confirming the existence of the non-noble metal in the

metallic state as expected from the formation of the Pt_xM alloy. For such purpose, only acid-washed samples are relevant, given that water-washed samples would mainly show the non-noble metal as oxide as result of the air exposure, even though it could be in the metallic state subsurface. Alternatively, acid-washing the catalysts causes the leaching of the non-noble metal from the outermost surface layers of the nanoparticles and therefore only the metallic state should be detected (note that non-leachable species could still remain after washing, i.e. carbides). The downside is that this limits the quantification of the atomic ratio by decreasing the signal of non-noble metal.

10

X-ray photoelectron spectroscopy (XPS) measurements were acquired under ultra-high vacuum (UHV) conditions ($< 10^{-9}$ millibar) in a Theta-Probe instrument (Thermo Scientific). This instrument is equipped with a monochromatized Al K α source (emission line at 1486.7 eV), and XPS spectra were obtained at an analyzer pass energy of 100 eV. In all cases, the atomic concentrations were quantified by integration of the Pt 4f, M 3d/4d (M = Y, Gd, Tb), O 1s, C 1s peaks after removal of a Shirley-type background. The samples were mounted on carbon tape attached to aluminum foil for a better contact. Reference XPS spectra for comparison were obtained from the NIST X-ray Photoelectron Spectroscopy Database and in-house measurements on polycrystalline alloy stubs from MaTeck®.

15
20

Example 10: Electrochemical characterization of the Pt_xM/C (M = Y, Gd, Tb)

25 catalysts

Water-washed or acid-washed Pt_xM/C catalysts were subjected to electrochemical testing by preparing drop-casted thin-film electrodes. Such electrodes were prepared by ultrasonic dispersing catalyst into an ink consisting of mainly ultra-pure water and absolute ethanol or isopropanol (in both cases 99.8%, Sigma-Aldrich, puriss. p.a., ACS Reagent). Small amounts of 2 wt.% polyvinylpyrrolidone (PVP, Sigma-Aldrich) in ethanol was added to help disperse the nanoparticles in the ink and Nafion perfluorinated resin solution (Sigma-Aldrich, 5 wt.% in mixture of lower aliphatic alcohols and water) was added to improve adhesion to the glassy carbon.

30

A representative catalyst ink formula used for electrochemical testing contains 5 mg of carbon-supported catalyst with 50 wt.% Pt loading, 1,4 mL of ultra-pure water, 5 mL of ethanol (or isopropanol), 15 μL of 2 wt.% PVP solution and 20 μL of 5 wt.% Nafion solution. When used for drop-casting 5 mm diameter glassy carbon electrodes (Pine Instruments), 10 μL of such ink yield electrodes with a Pt loading of $\sim 14 \mu\text{g cm}^{-2}$, and mass fraction of catalyst, Nafion and PVP of 80 wt.%, 19 wt.% and 1 wt.%, respectively.

The glassy carbon disks were polished beforehand using Buehler MicroPolishTM 0.05 mm alumina particles on a Buehler MicroCloth PSA and then ultra-sonicated twice in both isopropanol and deionized water. The electrodes were prepared by first mounting the polished and cleaned glassy carbon disk in a custom-made Teflon holder, and then drop-casted with the prepared ink on a glassy carbon disk, while measuring the mass of the droplet to accurately calculate the Pt mass on the electrode. The deposited aliquot is allowed to dry on air (or under a lamp heating up to 40-50 °C) and then the electrode is coupled to a Pine Instruments rotating-disk electrode Teflon shaft that was attached to a rotator device (also from Pine) provided with a rotation speed controller upon the electrochemical measurement.

20

The electrochemical characterization was carried out in a custom-made three-electrode glass cell provided with an external jacket attached to a water bath with temperature control. Prior to the measurement, the cell was cleaned in piranha solution (98% H_2SO_4 (Merck, Emsure) and 30% H_2O_2 (Merck, Emsure), 3:1 v/v) for at least 24 h and then cleaned several times in 18.2 $\text{M}\Omega \text{ cm}$ Millipore water at 85–90 °C to remove possible traces of the cleaning solution. The counter electrode was a Pt wire, and the reference was a $\text{Hg}|\text{Hg}_2\text{SO}_4$ electrode, the latter being separated from the working electrode compartment using a ceramic frit. The electrolyte, 0,1 M HClO_4 , was prepared using high-purity 70% HClO_4 (Merck, Suprapur) and ultrapure water (Millipore Milli-Q, resistivity $>18,2 \text{ M}\Omega \text{ cm}$, TOC $< 3 \text{ ppb}$). The gasses used were supplied by AGA with Instrument 5.0 purity for Ar, N_2 and O_2 gasses; Instrument 4.5 for the H_2 gas and Instrument 3.7 for the CO. All the measurements were carried out at $23 \pm 1 \text{ }^\circ\text{C}$ and the potential referred to the reversible hydrogen electrode (RHE) measured in the same electrolyte and corrected for ohmic drop (electrolyte resistance).

In each electrochemical measurement, the electrode was immersed into the electrochemical cell under potential control at 0.10 V in N₂-saturated 0,1 M HClO₄ electrolyte and subjected to potential cycling between 0,05 V and 1,00 V at 200 mV s⁻¹ until a stable cyclic voltammogram was achieved. Following this, the ORR performance of the Pt_xM/C catalysts was evaluated by means of hydrodynamic voltammetry in O₂-saturated solution at 50 mV s⁻¹.

After the ORR experiment, CO-stripping analysis was carried out for determining the electrochemical surface area (ECSA). For this purpose, CO gas was first bubbled into the electrolyte for 2 min, while the working electrode potential was kept at 0,05 V; then, the remaining CO dissolved in solution was removed by sparging Ar for 15 min whereas keeping the potential control. Afterwards, the potential was scanned up to 1.00 V in CO-free Ar-purged solution at 50 mV s⁻¹. The corresponding electrochemical active surface area (ECSA) of the Pt_xM/C catalysts was estimated assuming a ratio of 420 μC cm⁻².

References

1. W. L. F. Armarego and C. L. L. Chai, *Purification of Laboratory Chemicals*, 6th ed. Elsevier, 2009
- 20 2. M. Escudero-Escribano, A. Verdaguer-Casadevall, P. Malacrida, U. Grønbjerg, B. P. Knudsen, A. K. Jepsen, J. Rossmeisl, I. E. L. Stephens, and I. Chorkendorff, "Pt₅Gd as a highly active and stable catalyst for oxygen electroreduction.," *J. Am. Chem. Soc.*, vol. 134, no. 40, pp. 16476–9, Oct. 2012.
- 25 3. I. E. L. Stephens, A. S. Bondarenko, L. Bech, and I. Chorkendorff, "Oxygen Electroreduction Activity and X-Ray Photoelectron Spectroscopy of Platinum and Early Transition Metal Alloys," *ChemCatChem*, vol. 4, no. 3, pp. 341–349, Mar. 2012.

Claims

1. A process for preparing nanoparticles of an alloy comprising a noble metal and a non-noble metal, said process comprising the step of reacting a noble metal precursor and a non-noble metal precursor at a temperature in the range 300 to 1200 °C in the presence of a hydrogen source, wherein the reaction is subjected to a gas flow for removing volatile species;
 wherein said noble metal is selected from the group consisting of platinum, palladium, gold, and mixtures thereof, and said non-noble metal is selected from the group consisting of scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, and mixtures thereof;
 wherein said noble metal precursor comprises said noble metal in metallic form or a salt containing said noble metal in oxidized form;
 wherein said non-noble metal precursor comprises a salt containing said non-noble metal in oxidized form;
 wherein the one or more counterion(s) of said salt containing said noble metal in oxidized form and of said salt containing said non-noble metal in oxidized form form(s) a volatile species upon reaction with hydrogen, said volatile species being in gas form at the reaction temperature;
- 20 wherein said hydrogen source comprises hydrogen gas (H₂) and/or a species that releases hydrogen gas at the reaction temperature; and
 wherein the gas in said gas flow comprises hydrogen gas, an inert gas, or a mixture thereof.
- 25 2. The process according to claim 1, wherein said one or more counterion(s) are independently selected from halides, organic ligands, said organic ligands selected from the group consisting of N,N'-di-isopropylformadinate, N,N-bis(trimethylsilyl)amide, methylcyclopentadienyl, cyclopentadienyl, butylcyclopentadienyl, n-propylcyclopentadienyl, ethylenediamine, 1,5-cyclooctadiene, benzonitrile, pyridine, tetramethylcyclopentadienyl, 1,2-diaminocyclohexane, 2,5-Norbornadiene, acetonitrile, 1,4,7-trimethyl-1,4,7-triazacyclononane, methyl, pentamethylcyclopentadienyl, phenyl, 2,4-dimethylpentadienyl, cycloheptene, neomenthylcyclopentadienyl, 1,3-bis(trimethylsilyl)Cyclopentadienide, 2,3-dimethylquinoxaline, phenazine,

methylborabenzene, cyclooctatetraenyl; inorganic acid residues, and mixtures thereof.

3. The process according to claim 2, wherein said one or more counterion(s)
5 are halides.

4. The process according to claim 3, wherein said halide is selected from the group consisting of chloride, bromide, iodide, and mixtures thereof.

10 5. The process according to claim 4, wherein said halide is chloride.

6. The process according to any one of the preceding claims, wherein said non-noble metal is selected from the group consisting of yttrium, gadolinium, terbium, dysprosium, lanthanum, samarium, cerium, and mixtures thereof.

15

7. The process according to claim 6, wherein said non-noble metal is selected from the group consisting of yttrium, gadolinium, terbium, dysprosium, samarium, and mixtures thereof.

20 8. The process according to claim 7, wherein said non-noble metal is selected from the group consisting of yttrium, gadolinium, terbium, and mixtures thereof.

9. The process according to any one of the preceding claims, wherein said noble metal is platinum.

25

10. The process according to any one of the preceding claims, wherein said alloy is a binary, ternary, or quaternary alloy.

11. The process according to claim 10, wherein said alloy is a binary alloy.

30

12. The process according to any one of the preceding claims, wherein said hydrogen source is hydrogen gas, sodium borohydride, lithium borohydride, aluminum borohydride, ammonia, methane, ethane, propane, butane, pentane, *n*-hexane, cyclohexane, or hydrazine.

35

13. The process according to claim 12, wherein said hydrogen source is hydrogen gas.
14. The process according to any one of the preceding claims, wherein the gas
5 in said gas flow comprises hydrogen gas, helium, neon, argon, krypton, xenon, nitrogen, or a mixture thereof.
15. The process according to any one of the preceding claims, wherein the
reaction temperature is in the range 400 to 1100 °C, such as in the range 500 to
10 900 °C.

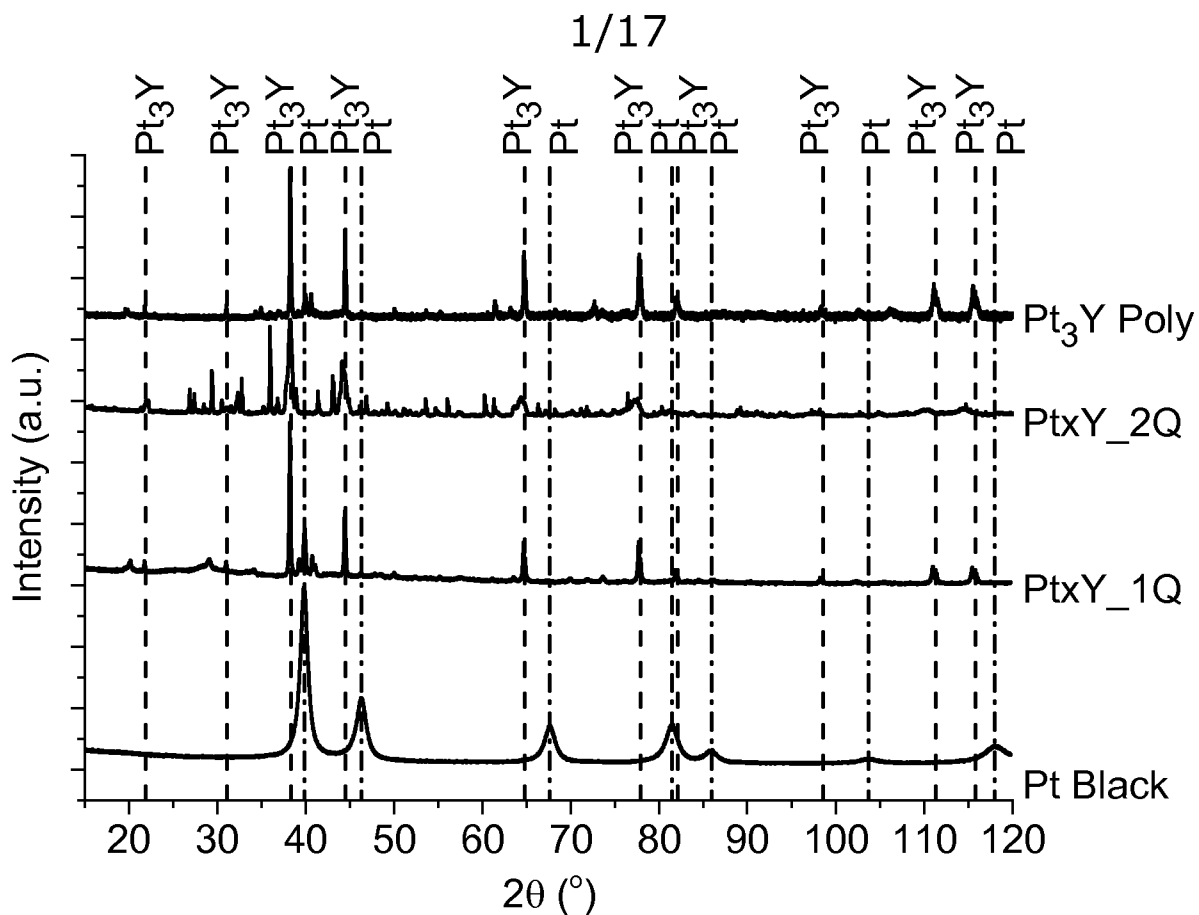
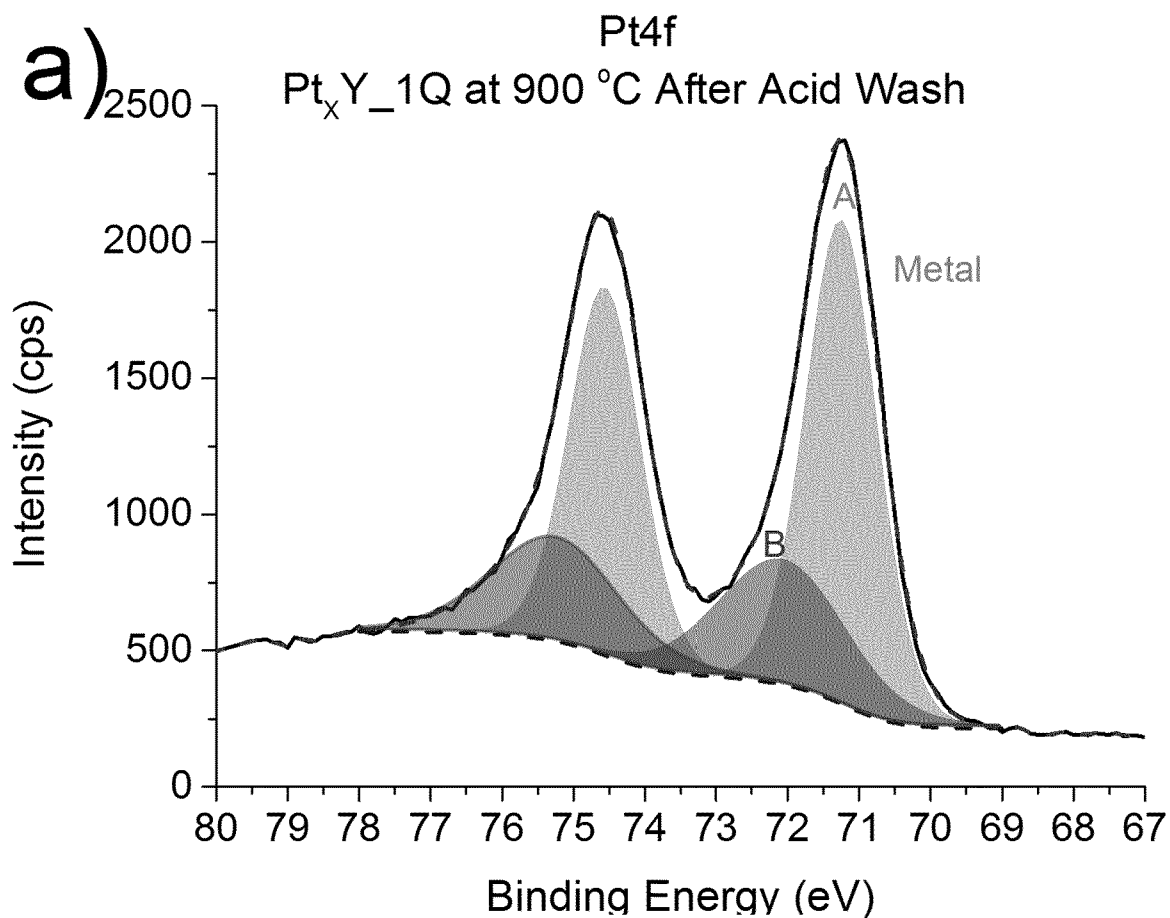
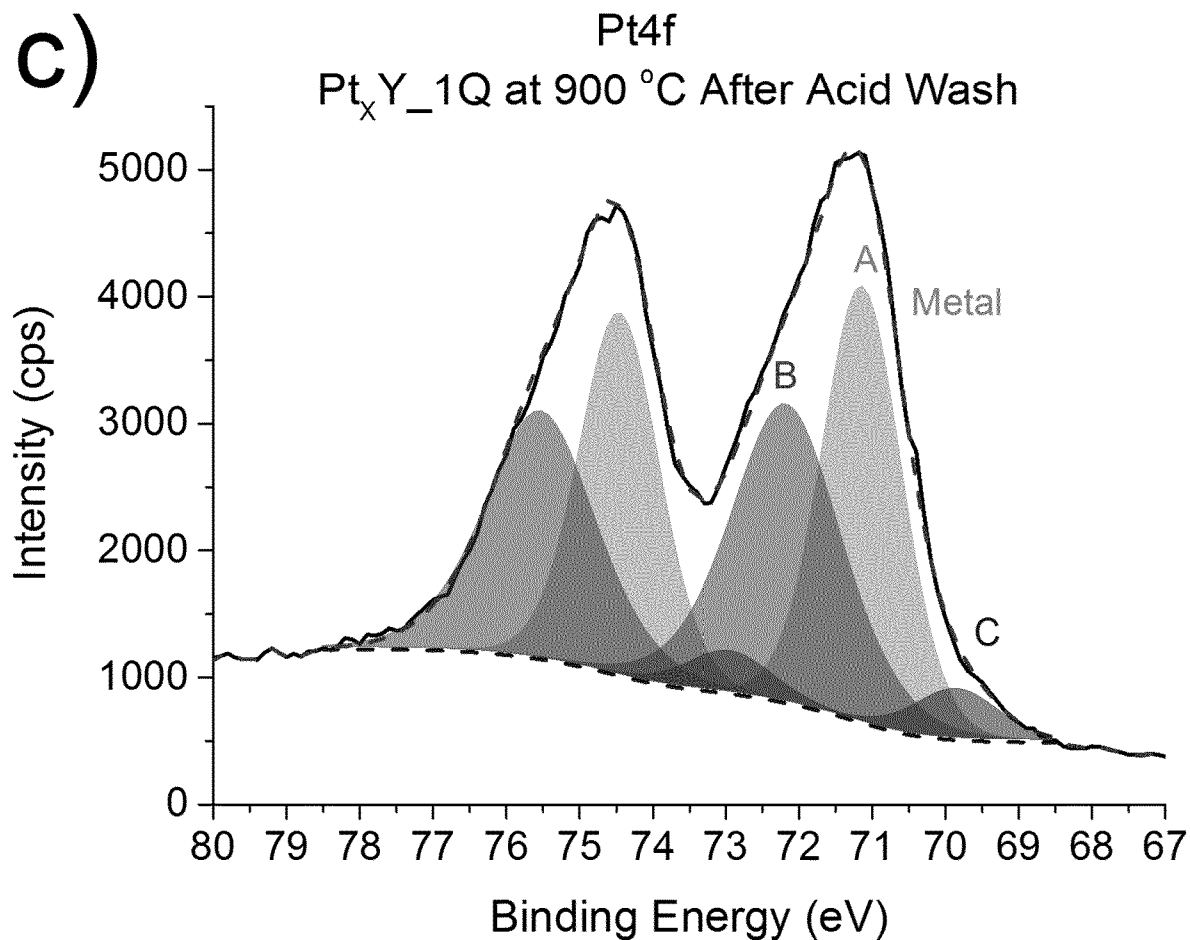
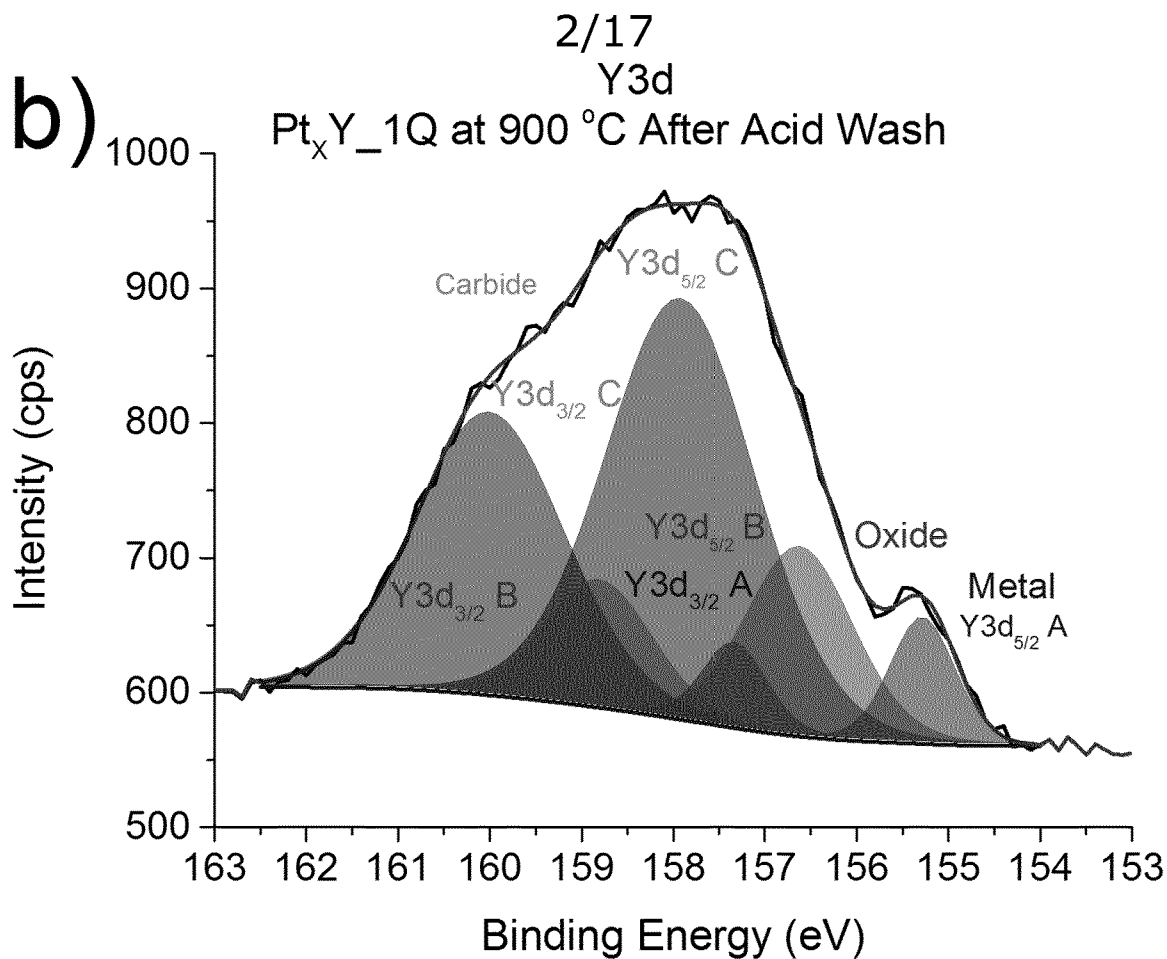


Fig. 1





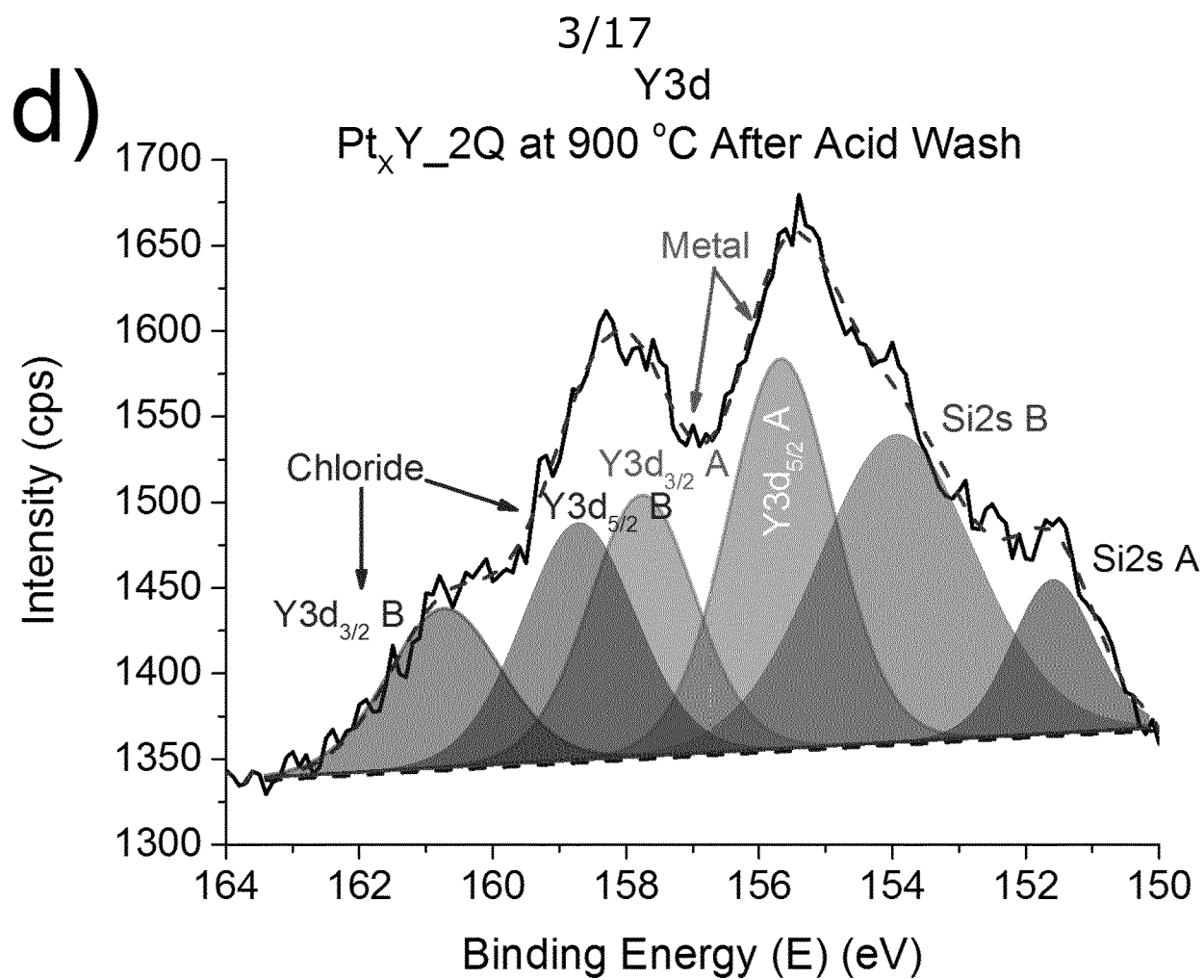


Fig. 2

4/17

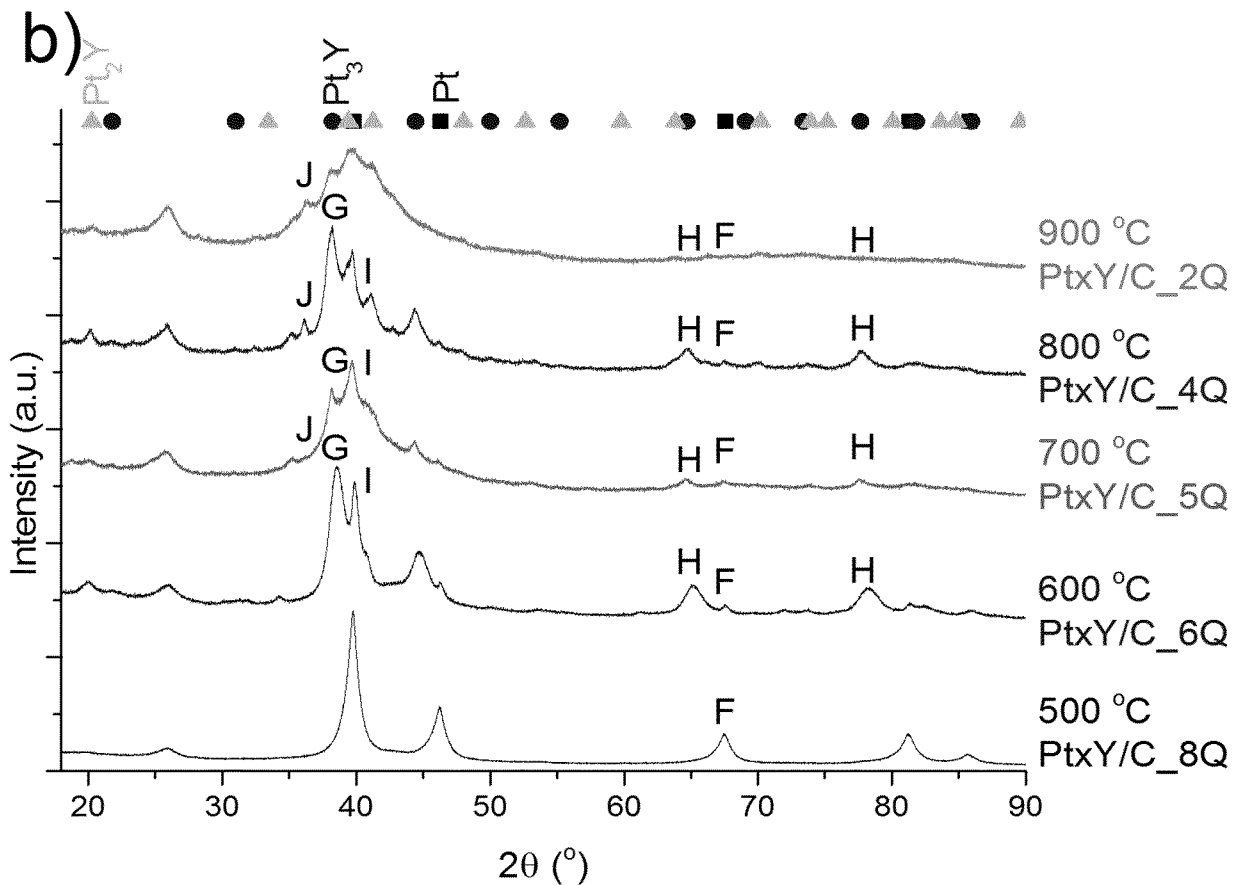
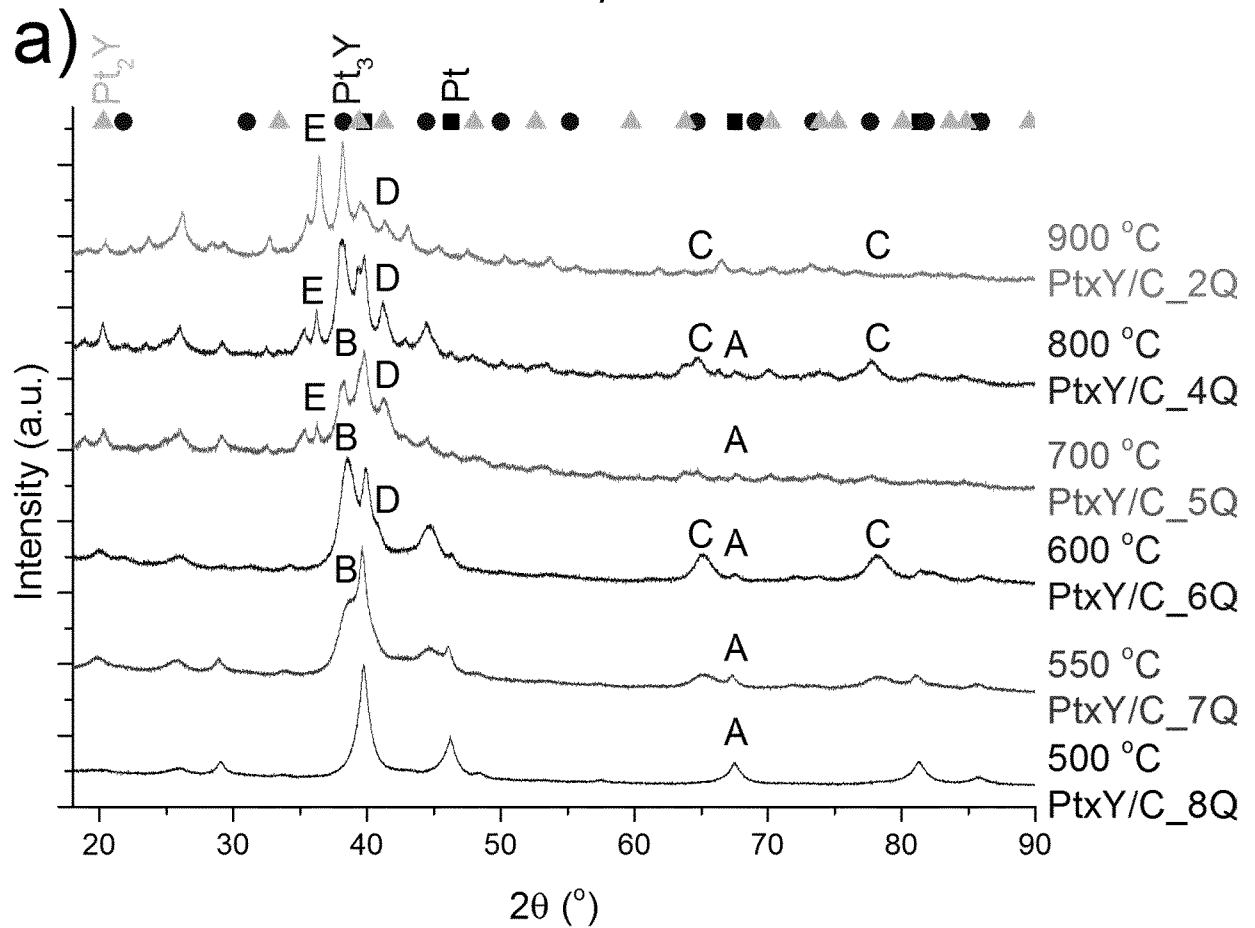


Fig. 3

5/17

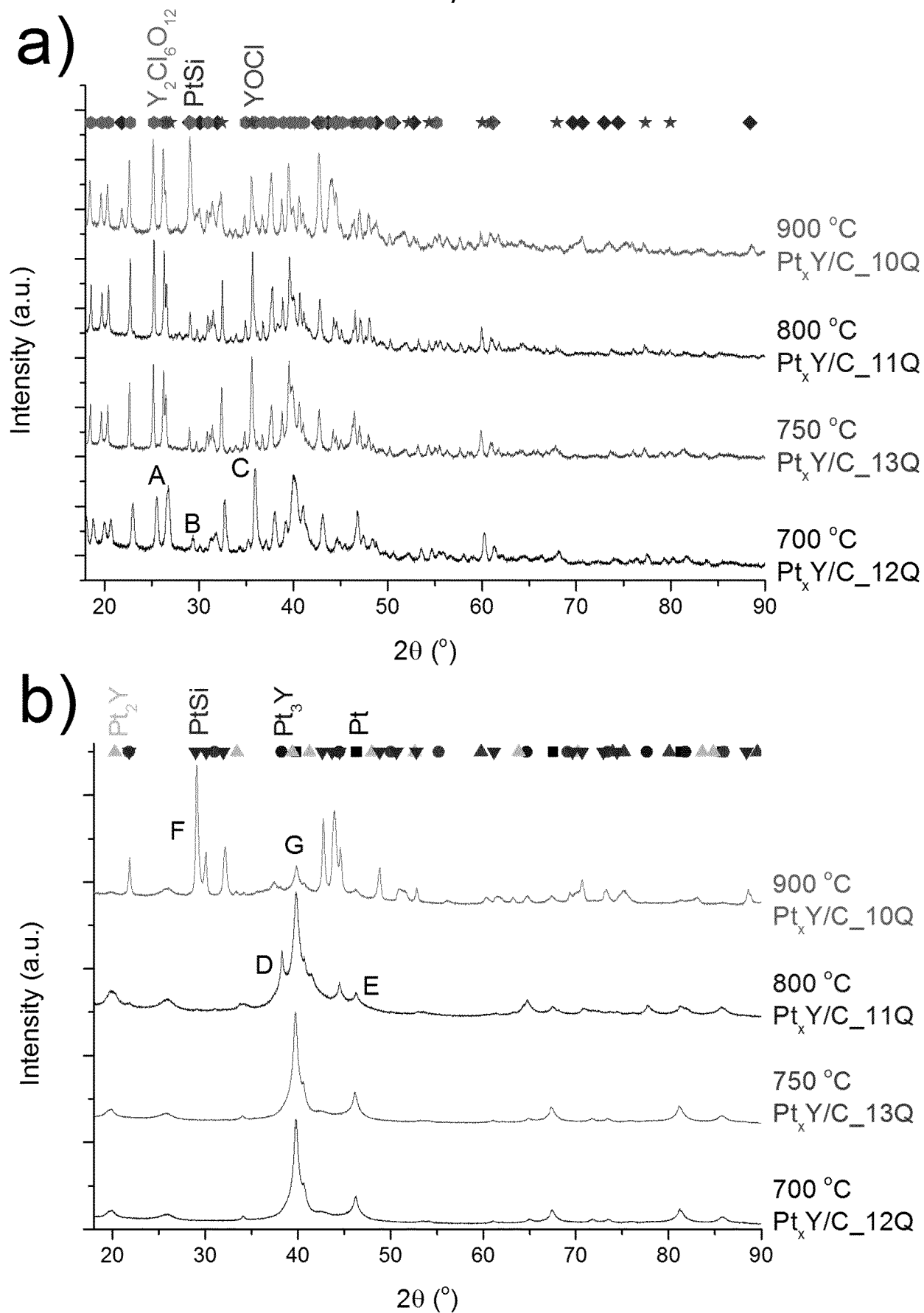


Fig. 4

6/17

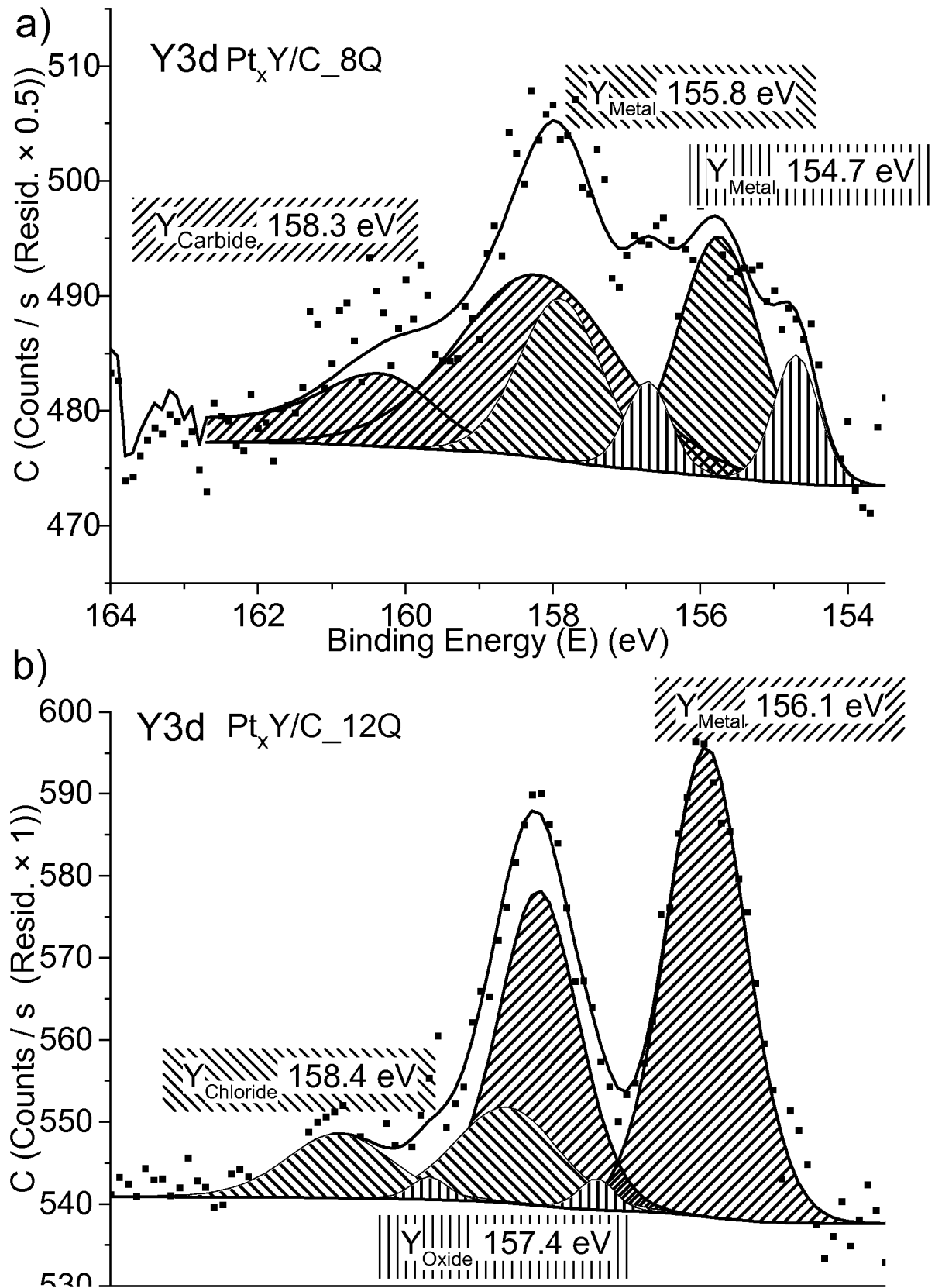


Fig. 5

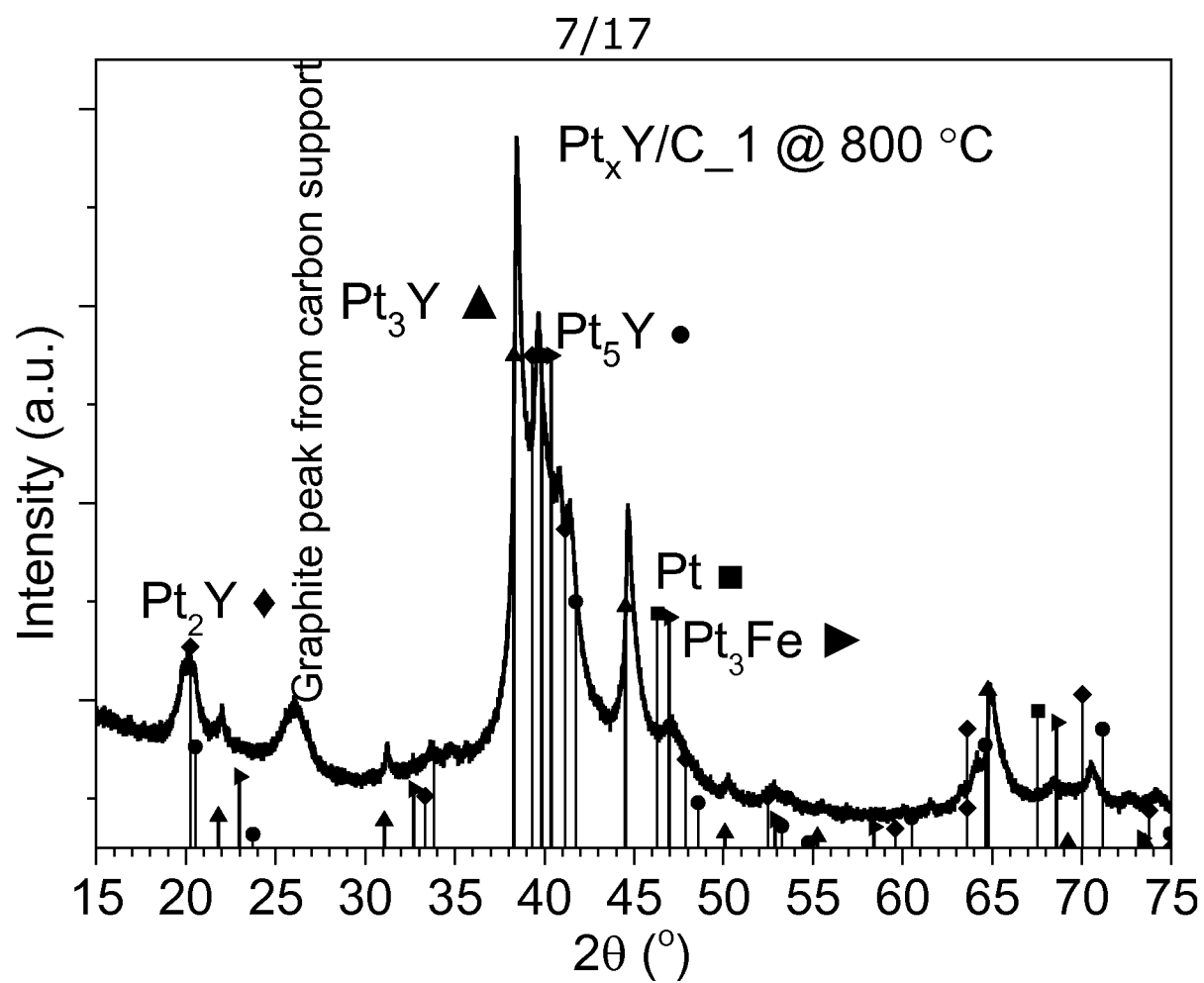


Fig. 6

8/17

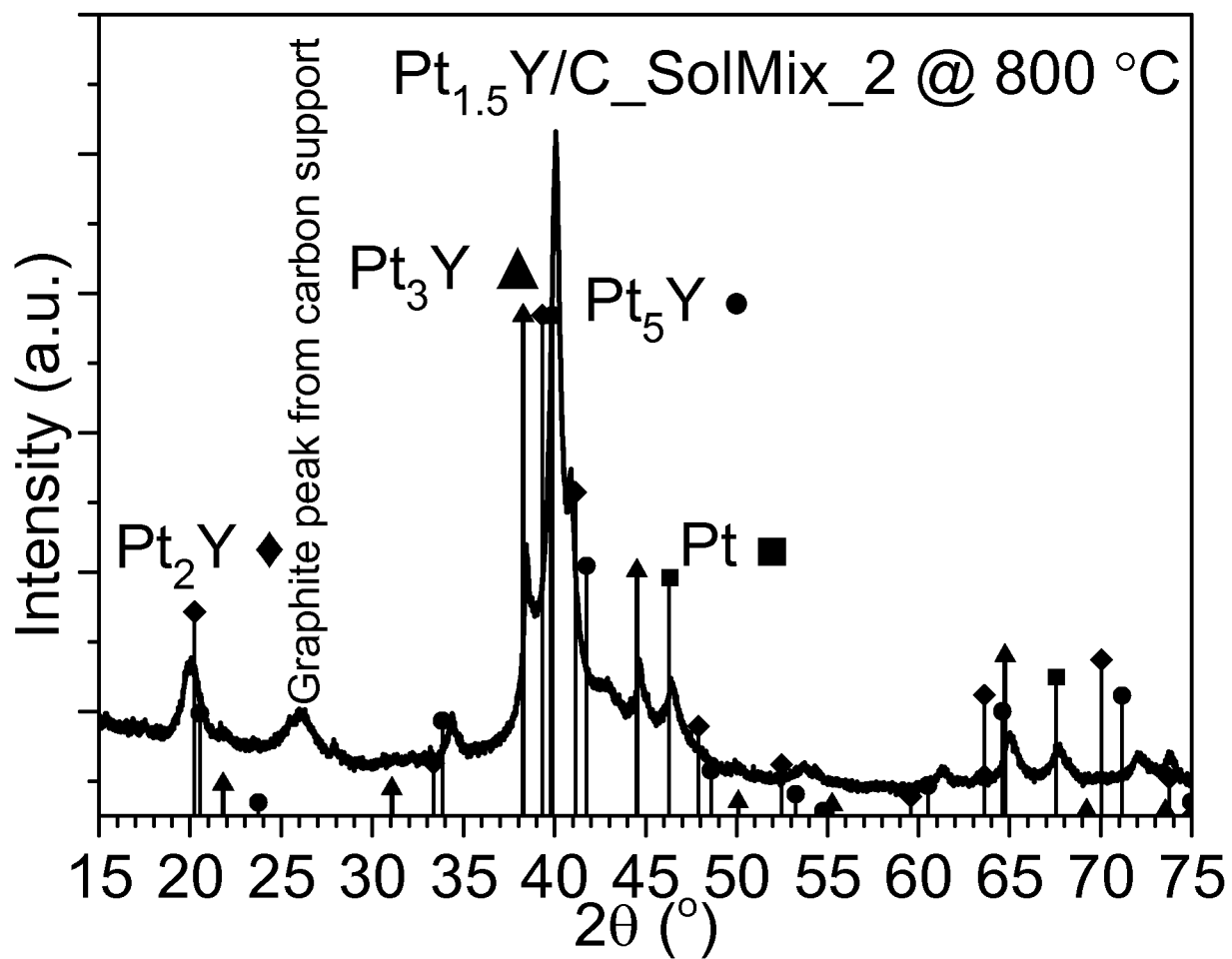


Fig. 7

9/17

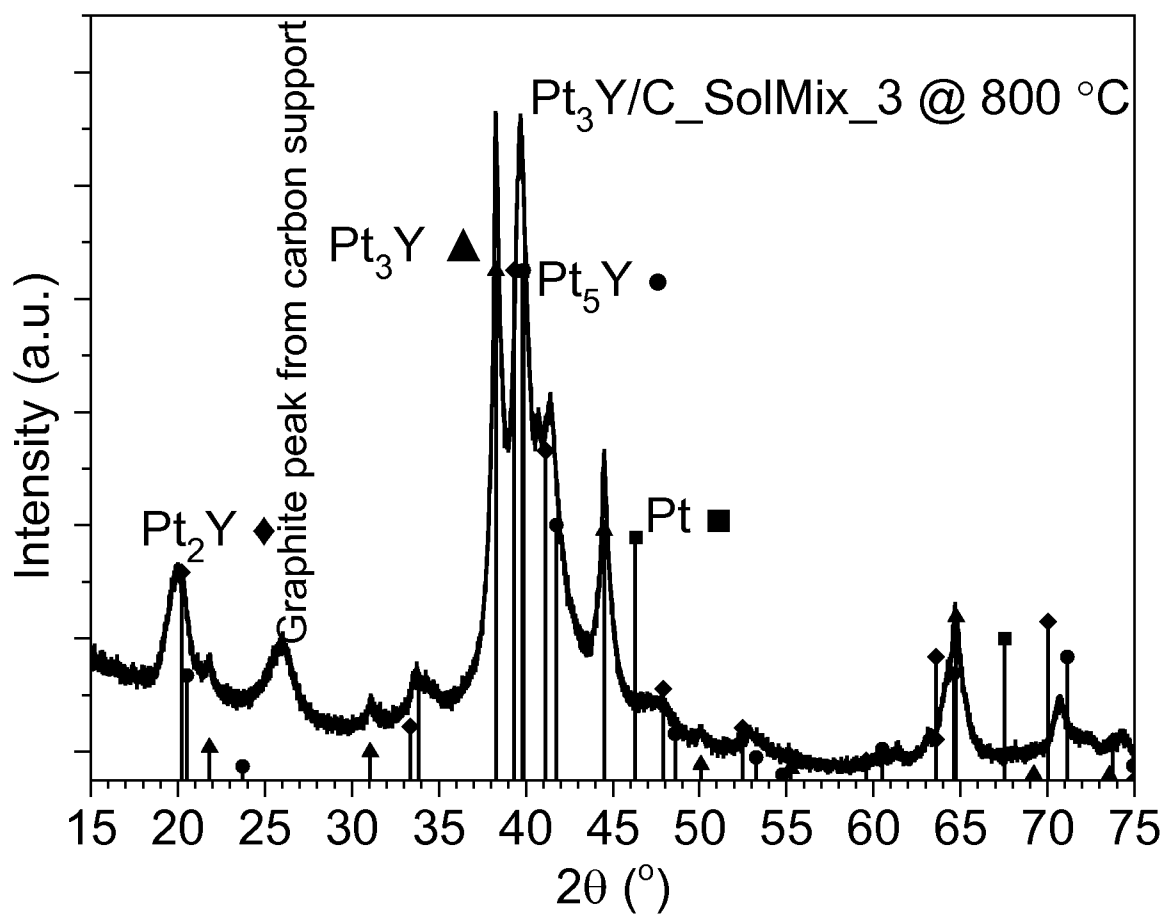


Fig. 8

10/17

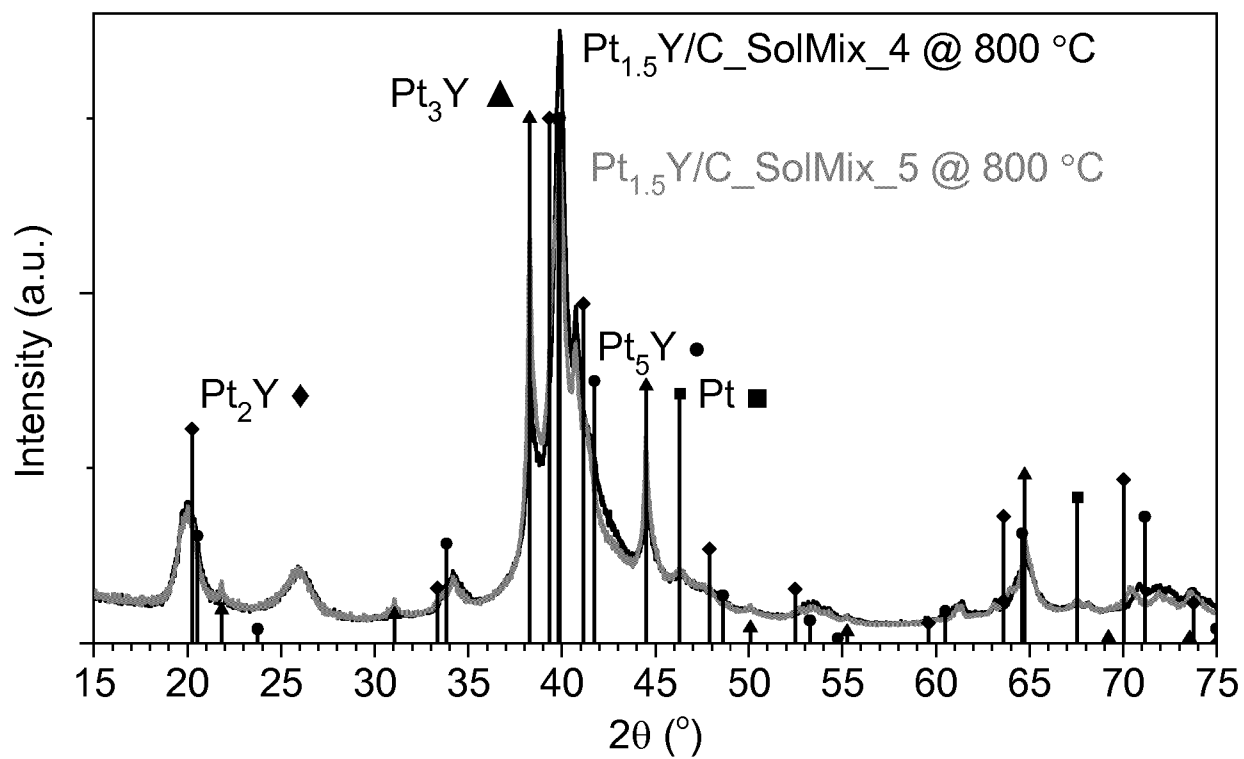


Fig. 9

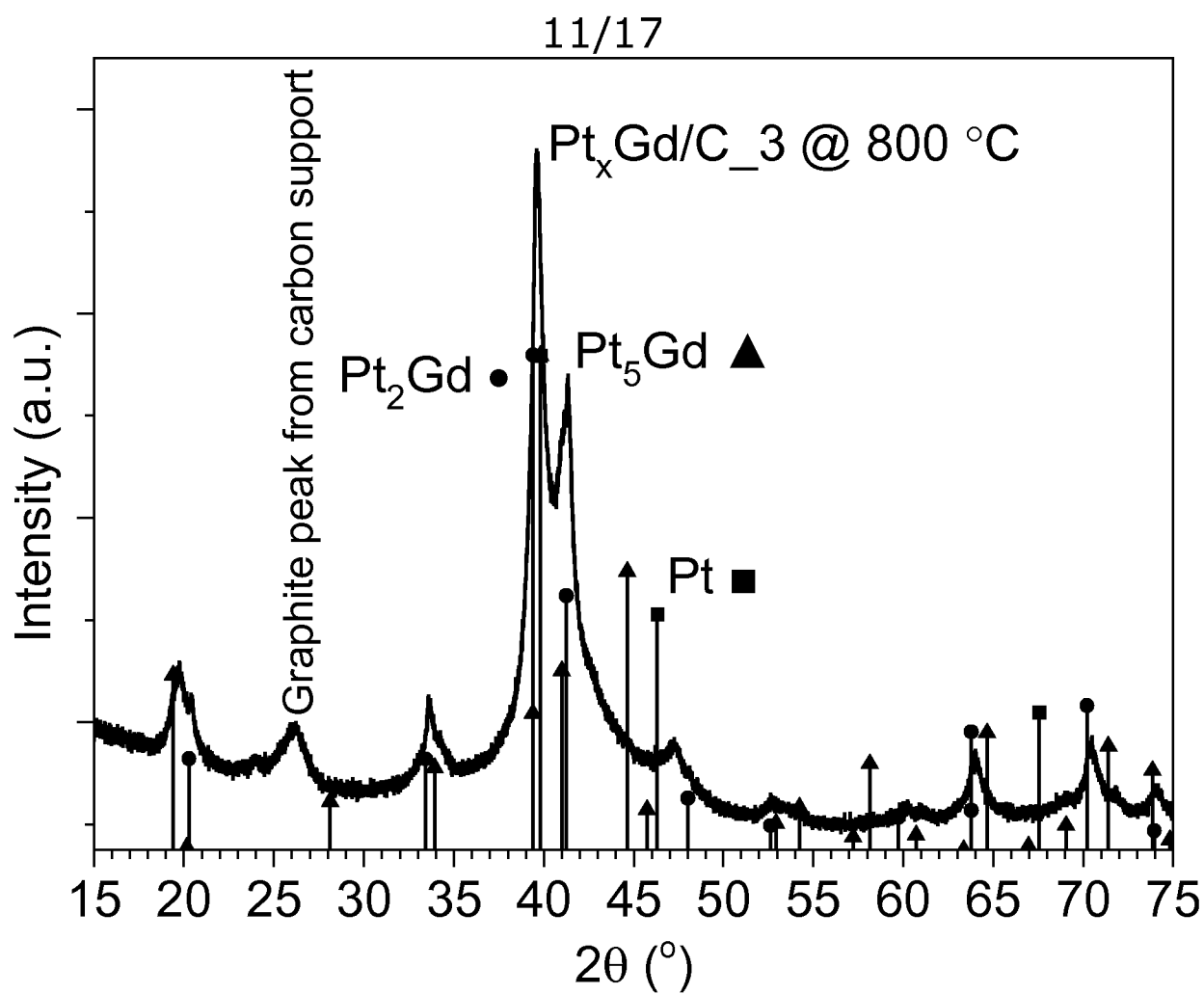


Fig. 10

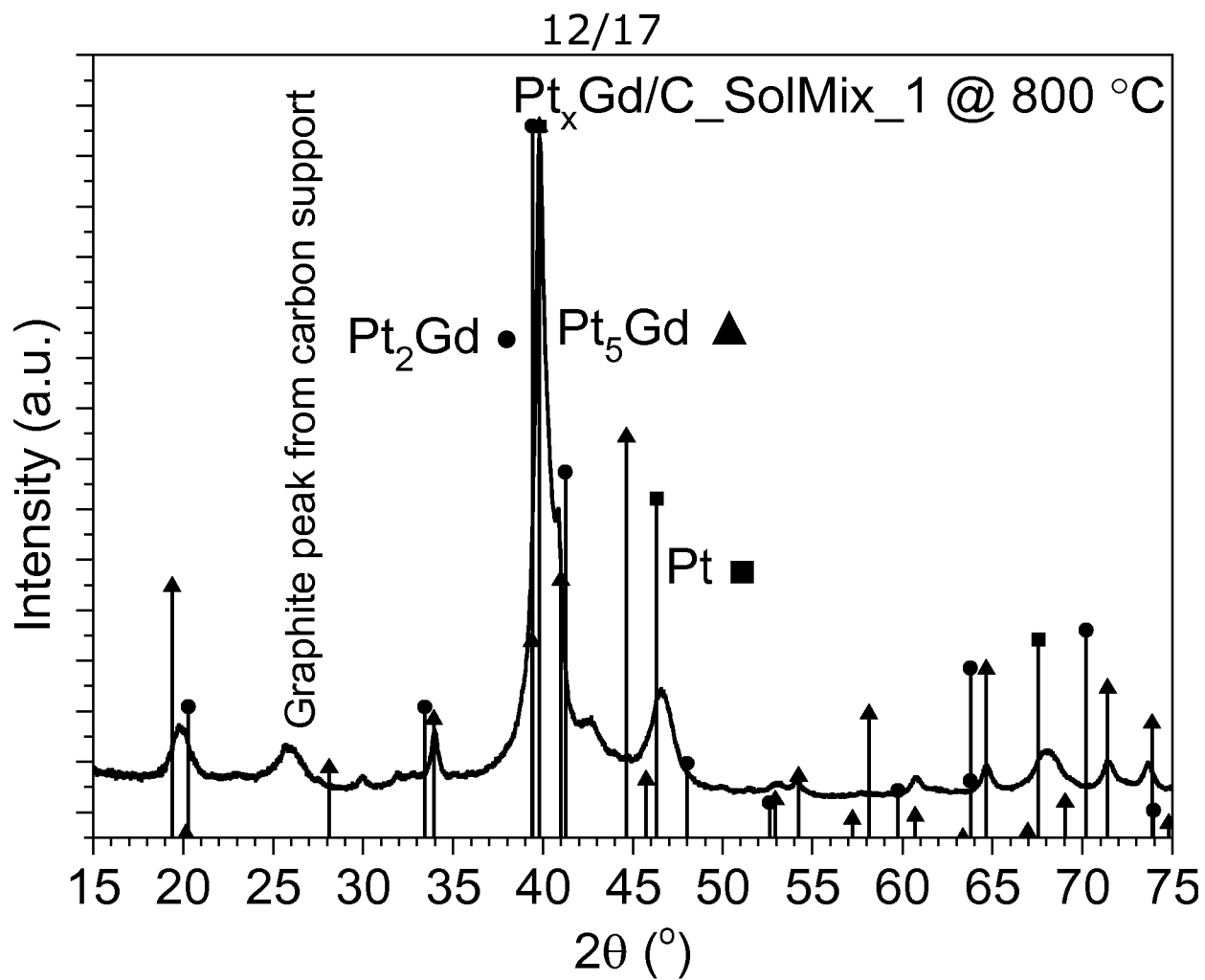


Fig. 11

13/17

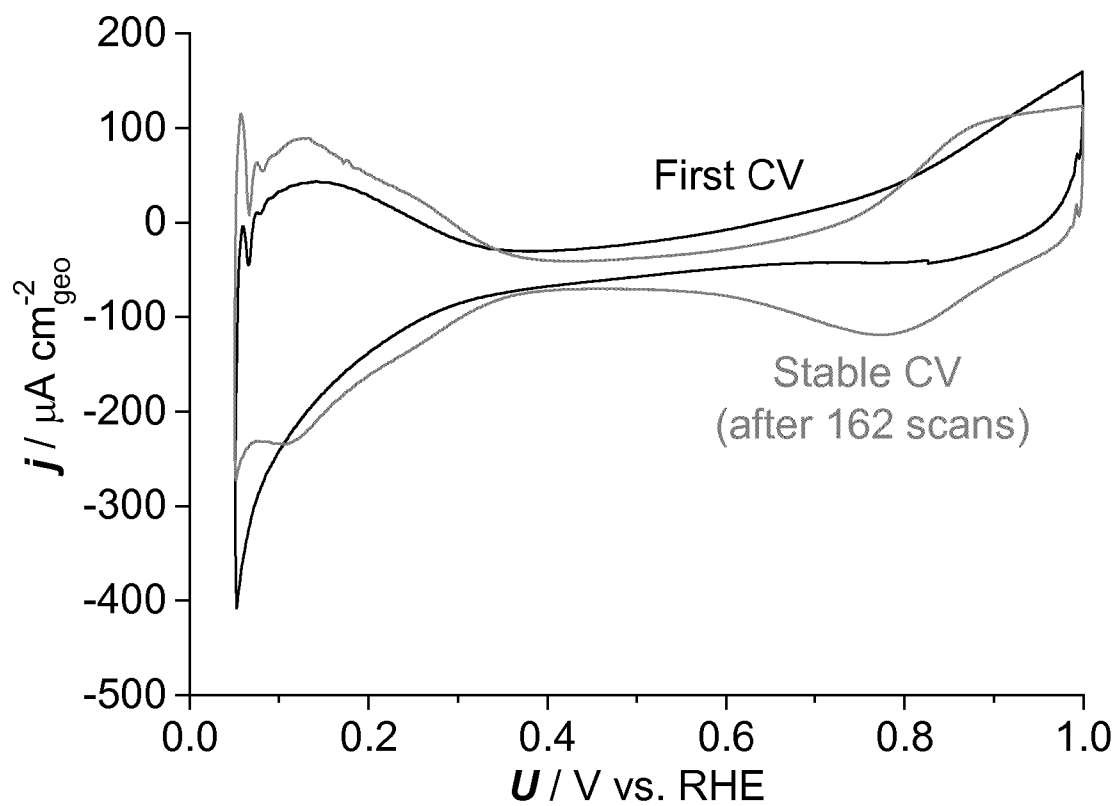


Fig. 12

14/17

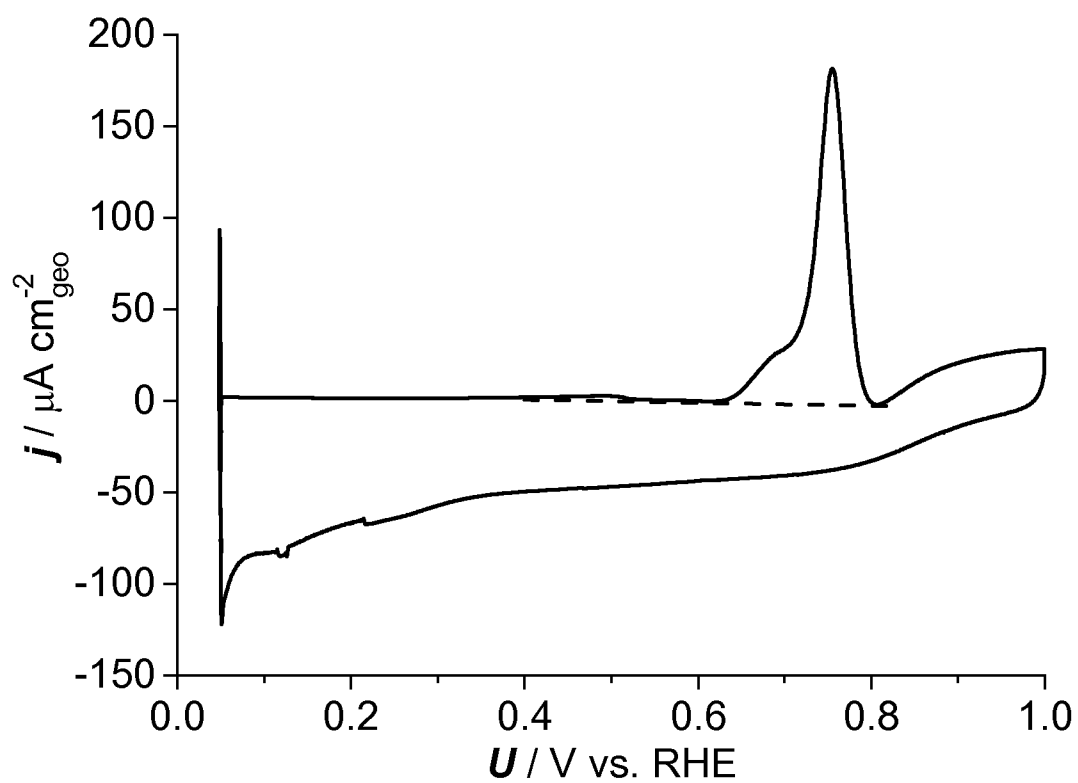


Fig. 13

15/17

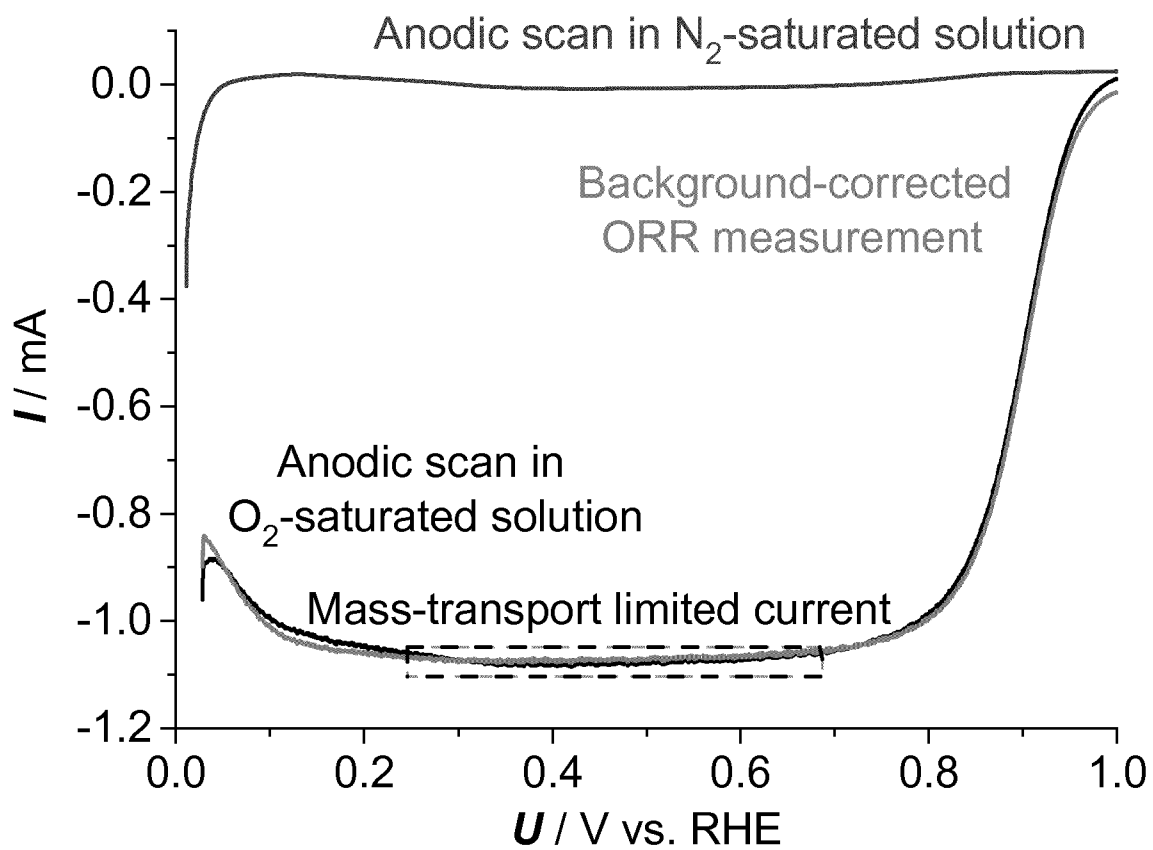


Fig. 14

16/17

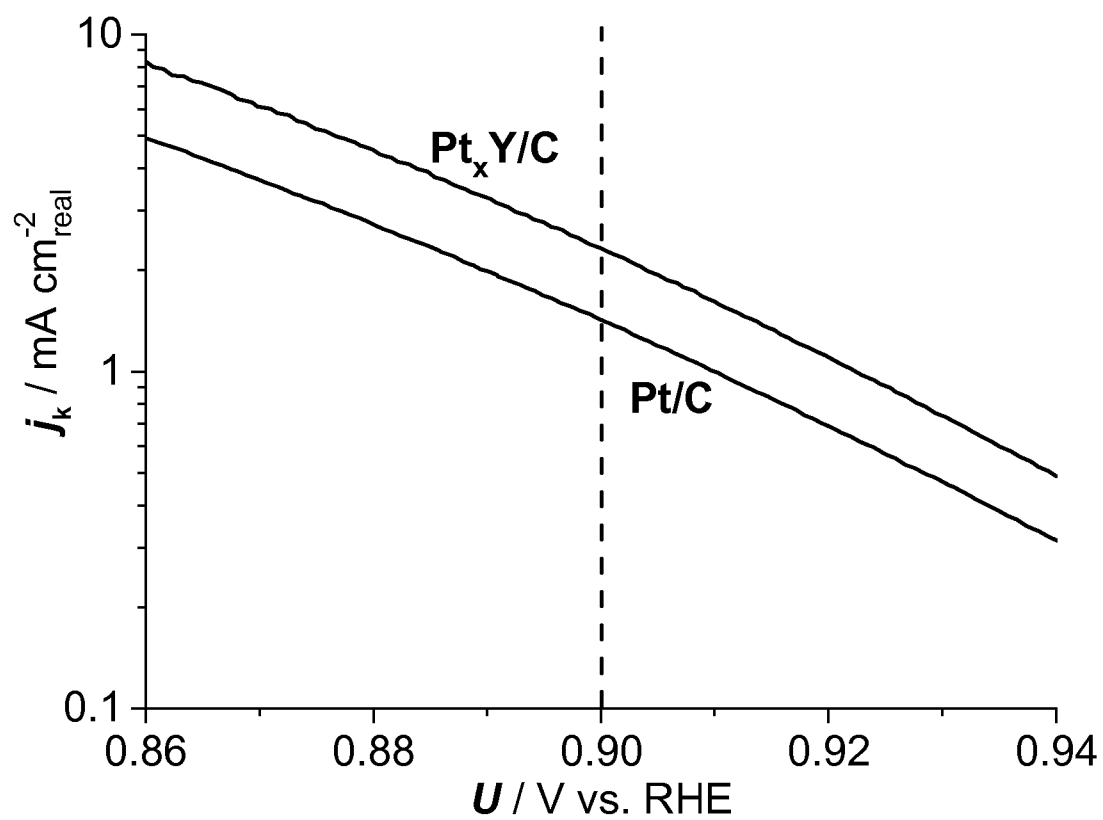


Fig. 15

17/17

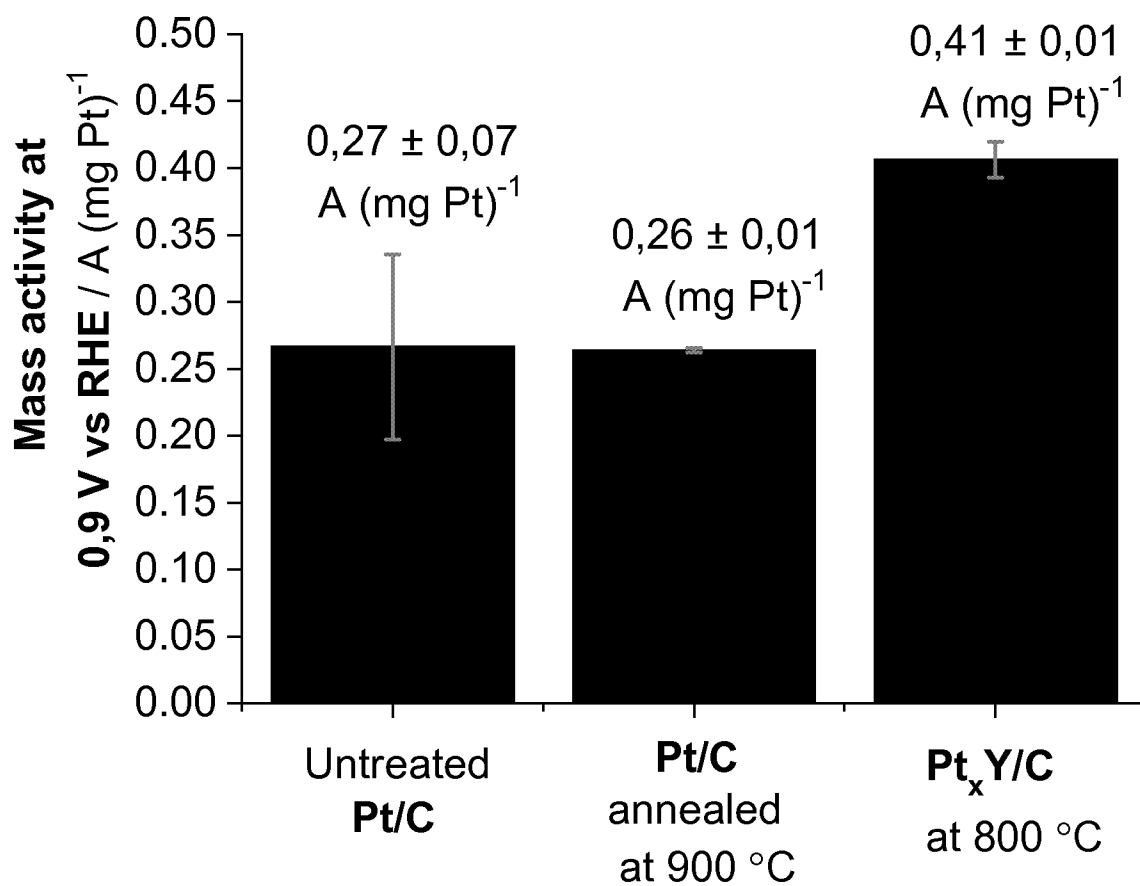


Fig. 16

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/060402

A. CLASSIFICATION OF SUBJECT MATTER

INV. B22F1/00 B22F9/20 B22F9/22 B22F9/24 B22F9/26
C22C1/04 B01J23/63 B01J23/66

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)

B22F C22C B01J

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, COMPENDEX, INSPEC, EMBASE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2015/144894 A1 (CENTRE NAT RECH SCIENT [FR]; UNIV POITIERS [FR]) 1 October 2015 (2015-10-01) page 5, lines 19-31 page 6, lines 29-30	1-15
A	----- US 2014/332721 A1 (ZHOU MINGJIE [CN] ET AL) 13 November 2014 (2014-11-13) the whole document	1-15
A	----- US 2015/080614 A1 (RAJARAM BAL [IN] ET AL) 19 March 2015 (2015-03-19) the whole document -----	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

30 June 2017

Date of mailing of the international search report

10/07/2017

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

Helgadóttir, Inga

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/060402

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2015144894 A1	01-10-2015	EP 3122688 A1 FR 3019169 A1 JP 2017510445 A US 2017133688 A1 WO 2015144894 A1	01-02-2017 02-10-2015 13-04-2017 11-05-2017 01-10-2015
US 2014332721 A1	13-11-2014	CN 104053749 A EP 2832819 A1 JP 5913730 B2 JP 2015514829 A US 2014332721 A1 WO 2013143102 A1	17-09-2014 04-02-2015 27-04-2016 21-05-2015 13-11-2014 03-10-2013
US 2015080614 A1	19-03-2015	NONE	