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(54) Benævnelse: **FREMGANGSMÅDE TIL FREMSTILLING AF UNDERSTØTTEDE PLATINPARTIKLER**

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METHOD FOR PREPARING SUPPORTED PLATINUM PARTICLES

Description

The present invention relates to the preparation of supported platinum particles which can be used as catalysts in fuel cells or electrolytic cells.

It is known that platinum particles which are applied to a substrate material such as carbon are used as catalysts for fuel cells (for example proton exchange membrane (PEM) fuel cells) or electrolytic cells (for example for water electrolysis). These supported catalyst compositions comprise as components the catalytically active material (platinum particle) and the substrate material, which is usually likewise present in the form of particles (e.g., carbon particles). The reactions catalyzed with this catalyst system are surface reactions. Therefore, the available platinum surface is of crucial importance and should be as large as possible (maximizing the accessible platinum surface). This implies that the platinum particles are to be made as small as possible in order to achieve the largest possible ratio of surface area to volume. However, as the particle size of these platinum particles decreases, the stability in the electrochemical environment used decreases. It is therefore necessary to make the platinum particles as large as necessary to achieve sufficient stability, but to keep them as small as possible to achieve a sufficiently high mass activity (i.e., a current standardized to the platinum mass at a given voltage).

To maximize the electrochemically active platinum surface area (sum of the electrochemically accessible surface area of all platinum particles), the platinum particles must be distributed as uniformly as possible and with a high degree of dispersion on the substrate. Furthermore, the synthesis conditions should be selected such that the platinum particles form very predominantly on the support, while the formation of unsupported platinum particle agglomerates is avoided as far as possible.

J.C. Meier et al., Beilstein J. Nanotechnol., 2014, 5, pp. 44-67 describe catalyst compositions for fuel cells which contain carbon as a substrate material and platinum particles. The properties of the carbon-supported platinum particles are summarized in Table 1. The particle sizes of the platinum particles were determined by means of TEM images. Because this method only takes into account a very limited number of platinum particles and, for example, platinum particles present in the pores of the substrate material are not reliably detected, TEM does not allow reliable determination of the particle size distribution of the platinum particles. According to Table 1 of the publication, mass activities of 0.32 A/mg Pt and 0.35 A/mg Pt were determined in the case of an average size of the platinum particles of 3-4 nm in $HClO_4$ as determined via TEM. In the case of a further reduction of the average particle size of the platinum particles to 1-2 nm, it was possible to achieve mass activities of more than 0.40 A/mg Pt. Due to the very small particle size, however, the stability of the platinum particles is reduced significantly.

A number of methods are known for the preparation of carbon-supported platinum particles; see, for example, the review article by K.B. Kokoh et al., Catalysts, 2015, 5, pp. 310-348. Platinum particles can be formed on a carbon support, for example, via the microemulsion method, the polyol method or a method in which the substrate is first impregnated with a platinum compound and this platinum compound is subsequently reduced to metallic platinum.

In the microemulsion method, surfactants are usually used which can be adsorbed on the surface of the platinum particles which form and have to be removed before the supported platinum particles are used as catalysts.

In the polyol method, the polyhydric alcohol (e.g., ethylene glycol) acts as both a solvent and a reducing agent. The oxidation of the polyol gives rise to compounds which interact with the surface of the platinum particles that are formed and therefore stabilize the particles. Before the supported platinum particles are used as catalysts, these adsorbed compounds must be removed by means of suitable treatment (e.g., thermal treatment or washing with an acid).

As already mentioned above, it is also known to first impregnate a carbon-based substrate material dispersed in an aqueous medium with a platinum compound acting as a precursor (impregnation step) and subsequently to reduce the platinum compound present on the substrate material to form metallic platinum (reduction step).

For the reduction step, the substrate material impregnated with the platinum compound can be removed from the aqueous medium and dried in order to subsequently be treated with a reducing gas such as hydrogen at a higher temperature. However, this can lead to an agglomeration of adjacent platinum particles and thus an undesired and difficult-to-control increase in particle size.

Alternatively, the platinum compound present on the substrate material can already be reduced in the aqueous medium. For example, $NaBH_4$, formic acid, hydrogen (H_2), sodium thiosulfate, formaldehyde or hydrazine can be used as reducing agents.

US 2006/0099483 A1 describes a method for preparing a substrate material to which catalyst particles can be applied. In this method, for example, an inorganic oxide such as SiOz is mixed with a carbon-based material (e.g., carbon black or activated carbon) and subjected to a heat treatment. Metallic particles can be applied to the substrate material obtained via an impregnating method with subsequent reduction. The inorganic oxide of the substrate material can be partially removed again via treatment with an acid or base.

US 2006/0159980 A1 describes a method for preparing supported platinum particles, wherein a platinum compound is brought into contact with a reducing agent and reduced to metallic platinum particles in a liquid medium in the presence of a cation-exchange polymer, and a substrate material (e.g., a carbon material) and a precipitant (e.g., an acid) are subsequently added to the liquid medium.

US 2008/0020924 A1 describes a method for preparing supported platinum particles as catalysts for fuel cells. The method is carried out in an ethylene glycol solution of which the water content is not more than 10 % by volume.

WO 2017/059192 A1 describes a method for preparing 2,5-dichloroaniline in the presence of supported platinum particles which act as hydrogenation catalysts. The supported platinum particles can be prepared in an aqueous medium.

It is an object of the present invention to prepare supported (i.e., present on a substrate material) platinum particles by means of a method which can be carried out easily and efficiently and distributes the particles on the support as uniformly as possible and with a high degree of dispersion, while the formation of unsupported, agglomerated platinum particles is avoided as far as possible. It is a further object of the present invention to provide a catalyst composition based on supported platinum particles which has good catalytic properties, in particular a high mass activity.

The object of the invention is achieved by a method for preparing a catalyst composition, wherein

(i) in an aqueous medium of which the water content is more than 50 vol.%, a substrate material in the form of carbon particles is impregnated with a platinum compound such that the platinum compound is absorbed on the surface of the carbon particles,

(ii) the impregnated substrate material is brought into contact, in the aqueous medium, with a reducing agent while stirring at a pH in the range of 3.5-6.0 and a stirrer Reynolds number of at least 50,000 such that metallic platinum particles are formed on the surface of the carbon particles.

In the context of the present invention, it has been found that a high dispersion level of metallic platinum particles on the substrate material can be realized with a very small proportion of non-supported platinum particles if both of the aforementioned conditions, i.e., a pH in the range of 3.5-6.0 and also a sufficiently high stirrer Reynolds number of at least 50,000 (i.e., sufficiently turbulent mixing of the aqueous medium), are maintained for the reduction step (ii). If one of these method parameters is not complied with, this can result in an uneven distribution of the metallic platinum particles on the substrate material and/or the formation of unsupported platinum particle agglomerates, as shown in the following examples.

As will be known to a person skilled in the art, the Reynolds number in the field of stirrer engineering (also known as the stirrer Reynolds number) represents a measure of how intensively a liquid medium is stirred. For values of the stirrer Reynolds number of more than 10,000, a liquid medium is considered to be turbulently mixed.

In the context of the present invention, this lower limit must still be significantly exceeded for turbulent mixing. In combination with the pH range according to the invention, this results in a very high degree of dispersion of the supported particles, while the formation of unsupported platinum particles is very effectively suppressed.

Suitable substrate materials in the form of carbon particles which can act as substrates for platinum particles are generally known to a person skilled in the art.

Carbon black (e.g., acetylene black), channel black, furnace black, lamp black or thermal black, activated carbon, pyrolytic carbon, graphite, a carbide-derived carbon, carbon nanotubes, graphene, mesoporous carbons, nitrogen or boron-doped carbons or a mixture of at least two of these carbon materials can be named as examples.

The carbon-based substrate material preferably has a high BET surface area in order to support the formation of finely dispersed platinum particles. The substrate material has, for example, a BET surface area of at least 10 m^2/g, more preferably at least 50 m^2/g or at least 150 m^2/g, for example 10-2000 m^2/g or 50-1500 m^2/g or 150-1300 m^2/g.

Optionally, the carbon-based substrate material can be porous. For example, the substrate material has a pore volume of at least 0.1 ml/g, more preferably at least 0.2 ml/g or at least 0.3 ml/g, for example 0.1-4.0 ml/g or 0.2-3.5 ml/g or 0.3-3.0 ml/g.

These substrate materials are commercially available or can be prepared by means of methods known to a person skilled in the art.

Platinum compounds which can be used for impregnating a substrate material and a subsequent reduction to metallic platinum are known to a person skilled in the art.

For example, the platinum compound is a Pt(II) or a platinum(IV) compound—for example, a Pt(II) or Pt(IV) salt or a Pt(II) or Pt(IV) complex or a Pt organometallic compound. Exemplary platinum compounds may be hexachloroplatinic acid or a salt of this acid, a platinum nitrate, a platinum halide, platinum acetylacetonate or platinum oxalate, or a mixture of at least two of these compounds.

If the metallic platinum particles to be prepared with the method according to the invention are to contain, in addition, an alloying element, one or more metal compounds can be added to the aqueous medium in addition to the platinum compound. In this case, the carbon particles acting as a substrate material are impregnated not only with the platinum compound, but also with the additional metal compound. This further metal compound can be, for example, a compound of one of the following metals: Ru, Pd, Ir, Cr, Co, Ni, Cu, Fe, Mn, W, V. This further compound can be, for example, a salt, a complex or an organometallic compound.

The aqueous medium preferably has a water content of more than 70 vol.%.

For the impregnation step, the carbon-based substrate material and the platinum compound to be deposited on the substrate material can be introduced into the aqueous medium simultaneously or in succession. For example, the substrate material is first dispersed in the aqueous medium, and the platinum compound is then added (for example, in the form of an aqueous solution).

Suitable conditions for impregnating the carbon-based substrate material with the platinum compound are known to a person skilled in the art. Preferably, the aqueous medium is stirred during the impregnation step. The stirrer power can be varied over a wide range. For example, the impregnation step can already be carried out at a stirrer Reynolds number of at least 50,000 or at least 75,000 or even at least 90,000 (e.g., 50,000-200,000 or 75,000-180,000 90,000-150,000). Alternatively, it is also possible to carry out the impregnation step at a stirrer Reynolds number of less than 50,000.

The pH of the aqueous medium during the impregnation step can be varied over a wide range. For example, during the impregnation step, the aqueous medium has a pH of at most 6.0.

During the impregnation step, the temperature of the aqueous medium is, for example, 20 °C-95 °C, more preferably 40 °C to 90 °C or 60 °C to 80 °C. The density and dynamic viscosity of water at this temperature T are used to determine the stirrer Reynolds number during step (i).

The mass ratio of the platinum present in the platinum compound to the substrate material is, for example, 1/10-8/10, and more preferably 2/10-7/10.

The substrate material is present in the aqueous medium, for example, in an amount of 0.05 wt.% to 2.5 wt.%, and more preferably 0.1 wt.% to 2.0 wt.%.

The duration of the impregnation step is selected such that the platinum compound can be deposited in sufficient quantity on the carbon particles acting as a substrate material. A suitable duration can be determined by a person skilled in the art on the basis of routine experiments.

During the impregnation step, the platinum compound is adsorbed on the substrate material, i.e., on the surface of the carbon particles. In the case of porous carbon particles, this can also be an inner surface, i.e., a surface within the pores. As a result of step (i), an impregnated substrate material is obtained.

As already mentioned above, in the reduction step (ii), the impregnated substrate material is brought into contact, in the aqueous medium, with a reducing agent while stirring at a pH in the range of 3.5-6.0 and a stirrer Reynolds number of at least 50,000.

As a result of the contacting with the reducing agent, metallic platinum particles are formed on the substrate material (i.e., on the surface of the carbon particles). The catalyst composition prepared by the method according to the invention comprises the metallic platinum particles, for example in an amount of 5-60 wt.%, more preferably 15-50 wt.% or 25-50 wt.%.

In the field of stirring technology, the stirrer Reynolds number represents a measure of how intensively a liquid medium is stirred. For values of the stirrer Reynolds number of more than 10,000, a liquid medium is considered to be turbulently mixed. The stirrer Reynolds number is determined at a temperature T_R in a known manner using the following formula:

$$R = (\rho * N * D^2)/\eta$$

wherein

R is the stirrer Reynolds number,

ρ is the density of water in kg/m^3 at the temperature T_R,

N is the speed of the stirrer in revolutions per second,

D is the maximum diameter of the stirrer,

η is the dynamic viscosity of water in kg/(m*s) at the temperature T_R.

The density and dynamic viscosity of water as a function of temperature are generally known. The maximum diameter D of the stirrer is determined perpendicular to the stirrer axis.

Common stirrers can be used to stir the aqueous medium during the reduction step (ii). Setting a sufficiently high stirrer speed ensures that the reduction takes place at a stirrer Reynolds number of at least 50,000. Examples of suitable stirrers that may be mentioned are anchor stirrers, screw stirrers, disk stirrers, impeller stirrers, propeller stirrers or pitched blade stirrers.

Step (ii) can be carried out in customary reactors known to a person skilled in the art.

Preferably, in step (ii), the ratio of the maximum stirrer diameter D to the maximum internal diameter $d_{reactor}$ of the reactor used in step (ii) is at least 0.4, more preferably at least 0.5 or at least 0.6. In a preferred embodiment, the following applies:

$$0.3 \leq D/d_{reactor} < 1.0;$$

more preferably the following applies:

$$0.4 \leq D/d_{reactor} \leq 0.98$$

or

$$0.5 \leq D/d_{reactor} \leq 0.90.$$

A suitable filling level for the aqueous medium with which the reactor is filled in step (ii) can be determined by a person skilled in the art on the basis of their general knowledge in the art. For example, the filling level H and the maximum internal diameter $d_{reactor}$ of the reactor satisfy the following condition:

$$0.5 \leq H/d_{reactor} < 2.0$$

Preferably, the same reactor and the same stirrer are used to perform steps (i) and (ii).

Formic acid, a metal borohydride (e.g., an alkali metal borohydride such as $NaBH_4$ and $LiBH_4$), an alkali metal hydride (e.g., sodium hydride), hydrogen (H_2), a metal thiosulfate (e.g., an alkali metal thiosulfate such as NaS_2O_3), an aldehyde (e.g., formaldehyde), an alcohol (e.g., a monohydroxy alcohol such as isopropanol), hydrazine, hydrazine hydrate, hydrazine hydrochloride, or ascorbic acid, or a mixture of at least two of these reducing agents can be used as the reducing agent.

Based upon their general knowledge in the art, a person skilled in the art can determine a suitable temperature T_R for the reduction step (i.e., a suitable temperature of the aqueous medium during the reduction step (ii)) as a function of the reducing agent that is used. The temperature T_R of the aqueous medium in step (ii) is, for example, in the range from 20 °C to 95 °C, more preferably 30 °C to 90 °C or 50 °C to 80 °C. The density and dynamic viscosity of water at this temperature T_R are used to determine the stirrer Reynolds number.

Preferably, the stirrer Reynolds number in step (ii) is at least 75,000, more preferably at least 90,000. In a preferred embodiment, the stirrer Reynolds number is 50,000-200,000, more preferably 75,000-180,000, even more preferably 90,000-150,000.

The pH of the aqueous medium in step (ii) is preferably in the range of 4.5-5.6, more preferably 4.9-5.3.

The reduction reduces the platinum compound present on the carbon particles acting as a substrate material to metallic platinum, and metallic nanoparticles are formed on the substrate material (i.e., on the carbon particles). If the substrate material has been impregnated with further metallic compounds, a platinum alloy can be obtained by reduction, for example a platinum alloy which contains one or more of the following metals: Ru, Pd, Ir, Cr, Co, Ni, Cu, Fe, Mn, W, V.

After reduction of the platinum compound to metallic platinum particles (which may be elemental platinum or a platinum alloy), the catalyst composition can be isolated from the aqueous medium by conventional methods and subjected to drying.

The method described above can be used to obtain a catalyst composition which has very good catalytic properties, in particular a very high mass activity.

The method described above can be used to obtain a catalyst composition comprising:

- a substrate material in the form of carbon particles,
- metallic platinum particles which are present on the substrate material and a volume-weighted particle size distribution, determined via small-angle X-ray scattering, with a d_{10} value ≥ 2.0 nm and a d_{90} value ≤ 7.0 nm.

In a preferred embodiment, the volume-weighted particle size distribution of the platinum particles has a median value d_{50} which is in the range of 3.0-5.0 nm, more preferably 3.5-4.5 nm.

Preferably, d_{10} is ≥ 2.0 nm and d_{90} is ≤ 6.5 nm, more preferably d_{10} is ≥ 2.3 nm and d_{90} is ≤ 6.0 nm.

Preferably, the d_{10}, d_{90} and d_{50} values of the particle size distribution of the platinum particles satisfy the following conditions:

$$(d_{90} - d_{10})/d_{50} \leq 1.0$$

Even more preferably, the following conditions apply:

$$0.5 \leq (d_{90} - d_{10})/d_{50} \leq 1.2$$

or

$$0.6 \leq (d_{90} - d_{10})/d_{50} \leq 0.9$$

The catalyst composition contains the metallic platinum particles, for example in an amount of 5-60 wt.%, more preferably 15-50 wt.% or 25-50 wt.%.

Preferably, the platinum particles contain no other metallic element, apart from unavoidable impurities (i.e., the platinum is present in elemental form). Alternatively, it is also possible for the platinum to be in the form of a platinum alloy. The platinum alloy can contain, for example, one or more of the following metals: Ru, Pd, Ir, Cr, Co, Ni, Cu, Fe, Mn, W, V.

With regard to the preferred properties of the carbon-based substrate material, reference can be made to the above statements.

Carbon black (e.g., acetylene black), channel black, furnace black, lamp black or thermal black, activated carbon, pyrolytic carbon, graphite, a carbide-derived carbon, carbon nanotubes, graphene, mesoporous carbons, nitrogen or boron-doped carbons or a mixture of at least two of these carbon materials can be named as examples of substrate materials.

The substrate material has, for example, a BET surface area of at least 10 m^2/g, more preferably at least 50 m^2/g or at least 150 m^2/g, for example 10-2000 m^2/g or 50-1500 m^2/g or 150-1300 m^2/g. Optionally, the substrate material can be porous. For example, the substrate material has a pore volume of at least 0.1 ml/g, more preferably at least 0.2 ml/g or at least 0.3 ml/g, for example 0.1-4.0 ml/g or 0.2-3.5 ml/g or 0.3-3.0 ml/g.

The catalyst composition preferably consists of at least 90 wt.%, more preferably at least 95 wt.% or even at least 98 wt.% of the carbon-based substrate material and the platinum particles.

The surface of the platinum particles is preferably free of surface-active substances.

The catalyst composition described above can be present in an electrochemical cell, in particular a fuel cell or electrolytic cell.

The fuel cell can be, for example, a proton exchange membrane (PEM) fuel cell, for example a hydrogen cell or a methanol PEM fuel cell. The electrolytic cell is preferably an electrolytic cell for the water electrolysis, in particular a PEM water electrolytic cell.

The composition described above can be used as a catalyst for an electrochemical reaction.

This electrochemical reaction is, for example, the electrochemical reduction of oxygen ("oxygen reduction reaction," ORR), the electrochemical oxidation of hydrogen ("hydrogen oxidation reaction," HOR), the electrochemical formation of oxygen from water ("oxygen evolution reaction," OER), or the electrochemical formation of hydrogen from water ("hydrogen evolution reaction," HER).

The measurement methods used in the present invention are specified below.

Reynolds number

The stirrer Reynolds number is determined at a temperature T_R using the following formula:

$$R = (\rho * N * D^2)/\eta$$

wherein

R is the stirrer Reynolds number,

ρ is the density of water in kg/m^3 at the temperature T_R,

N is the speed of the stirrer in revolutions per second,

D is the maximum diameter of the stirrer,

η is the dynamic viscosity of water in kg/(m*s) at the temperature T_R.

The density and dynamic viscosity of water as a function of temperature are generally known. The maximum diameter of the stirrer is determined perpendicular to the stirrer axis.

Determination of the pH

The pH was determined using a Mettler Toledo SevenCompact equipped with an InLab Reach Pro-425 electrode. Electrode type: pH combination electrode; diaphragm type: ceramic; reference electrolyte: 3 mol/l KCl; shank material: glass; reference electrode: Ag/AgCl.

The electrode is calibrated before the measurement.

Particle size distribution, d_{10}, d_{50} and d_{90} values

The particle size distribution was determined by means of small-angle X-ray scattering.

The X'Pert Pro "Bragg-Brentano" device is operated in transmission geometry, and the primary beam is provided with a mirror to generate a collimated beam. Catalyst material (10-20 mg) is applied between two Mylar films in a transmission sample carrier. A sample holder with the corresponding support material is required to determine the substrate. The source of radiation was a Cu X-ray tube with a standard excitation of 40 kV and 40 mA and with a wavelength of 0.1542 nm.

The scattering curves obtained after substrate stripping were evaluated by means of PANalytical EasySAXS software (ver. 2.0). Particle size distribution curves were calculated using algorithms implemented in this software. The principle consists in that the scattering curve I(q) resulting from the measurement is related to the particle size distribution DV(R) via the following integral:

$$I(q) = \int_{R=0}^{R=R_{Max}} D_V(R) \cdot R^3 \cdot I_0(q,R) dR$$

The symbols used are defined as follows:

q: scattering vector

Dv(R): volume-weighted particle size distribution

R: particle radius

Because the indirect Fourier transform from the equation above is very sensitive to noise in measurement data, the Dv(R) determination is performed using an iterative process. The distribution curve $D_V(R)$ resulting from this determination represents the volume-weighted particle size distribution (distribution by particle volume); this is related to the number-weighted particle size distribution $D_N(R)$ as follows:

$$D_V(R) \sim \frac{4\pi}{3} R^3 \cdot D_N(R)$$

To determine the particle size distribution with the Dv(R) function, it is assumed that an ensemble of homogeneous, non-interacting spherical particles is present. The algorithm uses an indirect Fourier transform, which is described in the following reference: D.I. Svergun et al., Acta Cryst., A44, 1988, pp. 244-250. No assumption is made about the shape of the distribution curve. A particle volume-weighted size distribution is obtained.

The particle size distribution of the platinum particles can be used to determine the d_{10}, d_{50} and d_{90} values. The d_x value indicates which volume-weighted proportion x (in %) of the particles is below this particle size.

<u>Measurement setup for electrochemical measurements</u>

The measurements of the electrochemical parameters such as mass activity and electrochemically active surface area were carried out by means of rotating disk electrodes (RDE).

All measurements were performed in a measuring cell with three Teflon containers in 0.1 M $HClO_4$ electrolyte solution at room temperature, using a Hg/Hg_2SO_4 reference electrode (Schott Instruments GmbH), a platinum network as a counter electrode and a potentiostat.

20 µl of an aqueous catalyst dispersion was applied to a sample body previously polished to a mirror finish with glass carbon substrate (diameter: 5 mm; 0.196 cm^2 Pine Research Instrumentation AFE5T050GC) and dried in an air atmosphere. The sample thus prepared had a noble metal loading of 14 $\mu g_{Pt} cm^{-2}$ and was attached to a rotating electrode (Pine Research Instrumentation AFMSRCE). Furthermore, all measurements, the determination of the ectrochemically active surface and the determination of the mass activity were carried out with compensated

electrolyte resistance. For this purpose, the mean value of the ohmic component of the electrolyte resistance before the measurement was determined at 4 kHz, 5 kHz, 6 kHz and compensated for with the "iR compenstaion" function of the potentiostat to a residual resistance of 2 ohms.

Determination of the electrochemical surface area (EASA)

The electrochemically-active surface area was determined from the measured charge of the hydrogen underpotential deposition. For this purpose, the polarization curves in argon-saturated electrolyte at a potential feed rate of 50 mVs^{-1} were used. The charge results after subtraction of the electrochemical double-layer capacitance from the integration of the current over time. A conversion factor of 200 μCcm^{-2} was used to determine the platinum surface area.

Determination of mass activity

The mass activity was determined from the anodic polarization curve in an oxygen-saturated electrolyte at a potential feed rate of 50 mVs^{-1} and a rotation rate of 1600 min^{-1} of the disk electrode after removal of the polarization curve in argon.

BET surface area

The BET surface area is determined by nitrogen sorption at 77 K using the BET method.

Pore volume

The pore volume is determined by nitrogen sorption at 77 K and a relative pressure $P/P_0=0.99$.

The present invention is explained in more detail with reference to the following examples.

Examples

Example 1

Impregnation step (i)

6 g of carbon black, commercially available as Vulcan® XC72-R with a BET surface area of approximately 250 m^2/g, was slurried with 100 ml of water, placed in a double-jacketed reactor and filled to 2 L with water. The stirrer Reynolds number was adjusted to 100,854 and the suspension was heated to 70 °C. After a holding time of 1 hour, 40 g of a nitric acid H_2PtCl_6 solution (10 wt.% Pt) were added and then kept for 1 hour under constant mixing and temperature.

Reduction step (ii)

By addition of Na_2CO_3, the pH of the aqueous medium was adjusted to a value of 5.1. This was followed by the addition of formic acid, which served as a reducing agent. The stirrer Reynolds number was 100,854 and the temperature of the aqueous medium was 70 °C. The ratio of the maximum stirrer diameter D to the maximum internal diameter $d_{reactor}$ of the reactor was 0.69. During reduction, the platinum compound present on the carbon particles was reduced to metallic platinum. This resulted in carbon particles on which metallic platinum particles are supported. After 0.5 hours, the catalyst composition was filtered off from the aqueous medium and dried at 110 °C under a nitrogen atmosphere. The platinum content of the catalyst composition was 40 wt.%.

TEM images of the catalyst composition were taken at various magnifications. These TEM images are shown in Fig. 1 and 2.

From Fig. 1, which shows only a few carbon particles at high magnification, it can be seen that the metallic platinum particles are distributed very homogeneously with a high degree of dispersion over the carbon particles acting as a substrate material.

From Fig. 2, which shows a significantly larger number of carbon particles compared to Fig. 1, it can be seen that the platinum particles are supported almost exclusively on the carbon particles. The formation of unsupported and agglomerated platinum particles was thus almost completely suppressed.

The process conditions of the reduction step and the properties of the supported catalyst composition as seen in the TEM images are summarized below in Table 1.

The particle size distribution of the platinum particles was determined by means of small-angle X-ray scattering. The particle size distribution was used to determine the d_{10}, d_{50} and d_{90} values. Furthermore, the electrochemically active surface area (EASA) and the mass activity were determined for the catalyst composition of example 1.

The results are summarized below in Table 2.

Comparative example 1

In comparative example 1, the catalyst composition was prepared under the same process conditions as in example 1, but with the following difference: during the reduction step (ii), the pH of the aqueous medium was 8.0. The stirrer and reactor of comparative example 1 corresponded to the stirrer and the reactor of example 1.

TEM images of the catalyst composition were taken at various magnifications. These TEM images are shown in Fig. 3 and 4.

From Fig. 3, which shows only a few carbon particles at high magnification, it can be seen that the metallic platinum particles present on the carbon particles have a significantly poorer degree of dispersion compared to the sample in example 1. From Fig. 4, which shows a significantly larger number of carbon particles compared to Fig. 3, it can be seen that the predominant proportion of the platinum particles is supported on the carbon particles.

The process conditions of the reduction step and the properties of the supported catalyst composition as seen in the TEM images are summarized below in Table 1.

The particle size distribution of the platinum particles was determined by means of small-angle X-ray scattering. The particle size distribution was used to determine the d_{10}, d_{50} and d_{90} values. Furthermore, the electrochemically active surface area (EASA) and the mass activity were determined for the catalyst composition of comparative example 1.

The results are summarized below in Table 2.

Comparative example 2

In comparative example 2, the catalyst composition was prepared under the same process conditions as in example 1, but with the following difference: during the reduction step (ii), the stirrer Reynolds number was 40,419. The stirrer of comparative example 2 corresponded to the stirrer of example 1, but was operated with another stirrer Reynolds number. The reactor of comparative example 2 also corresponded to the reactor used in example 1.

TEM images of the catalyst composition were taken at various magnifications. These TEM images are shown in Fig. 5 and 6.

From Fig. 5, which shows only a few carbon particles at high magnification, it can be seen that the metallic platinum particles present on the carbon particles have a high degree of dispersion. However, it can be seen from Fig. 6 that significant amounts of unsupported agglomerated platinum particles have formed.

The process conditions of the reduction step and the properties of the supported catalyst composition as seen in the TEM images are summarized below in Table 1.

Table 1: Process conditions of the reduction step and properties of the Pt particles

	Example 1	Comp. ex. 1	Comp. ex. 2
pH value during reduction step (ii)	5.1	8.0	5.1
Stirrer Reynolds number during reduction step (ii)	100,854	100,854	40,419
Degree of dispersion of the Pt particles on the carbon particles (from TEM image)	Very good	Medium	Very good
Fraction of unsupported Pt particles (from TEM image)	Very low	Low	Very high

As shown in Table 1, a high degree of dispersion of the supported platinum particles with almost complete avoidance of unsupported platinum particles is achieved only when both the pH and the stirrer Reynolds number are in the ranges according to the invention for the reduction step.

If the reduction is carried out at too low a stirrer Reynolds number, the platinum particles present on the carbon particles have a high degree of dispersion, but there is a significant proportion of unsupported platinum particles (i.e., not present on the carbon particles); see comparative example 2.

If the reduction was carried out at a very high Reynolds number (i.e., a number according to the invention) but the pH was not according to the invention, the proportion of unsupported Pt agglomerates can be kept relatively low, but the platinum particles supported on the carbon particles do not have a high degree of dispersion.

For the samples of example 1 and of comparative example 1 (i.e., the samples in which the platinum particles are predominantly present in a supported manner), the particle sizes of the platinum particles, the electrochemically active surface area and the mass activity were determined. The results are shown in Table 2.

Table 2: Particle sizes, EASA and mass activity of the Pt particles

	Example 1	Comp. ex. 1
d_{10} [nm]	2.6	3.0
d_{50} [nm]	3.8	5.3
d_{90} [nm]	5.2	19.0
$(d_{90}-d_{10})/d_{50}$	0.7	3.0
Electrochemically active surface area (EASA) [m^2/g]	65	50
Mass activity [A/g Pt]	464	374

The catalyst composition obtained by the method according to the invention was able to achieve a mass activity of significantly more than 400 A/g Pt. Despite this very high mass activity, the composition has only an extremely small proportion of very small Pt particles having a diameter of less than 2 nm (see d_{10} value in example 1), which has a positive effect on the stability of the Pt particles under the very corrosive conditions of a fuel cell or electrolytic cell.

PATENTKRAV

1. Fremgangsmåde til fremstilling af en katalysatorsammensætning, hvor

(i) et substratmateriale i form af carbonpartikler, i et vandigt medium, hvis vandindhold er mere end 50 vol-%, imprægneres med en platinforbindelse, således at platinforbindelsen adsorberes på carbonpartiklernes overflade,

(ii) det imprægnerede substratmateriale, i det vandige medium, bringes i kontakt med et reduktionsmiddel, mens der omrøres ved en pH-værdi i området på 3,5-6,0 og et omrører-Reynoldstal på mindst 50.000, således at der dannes metalliske platinpartikler på carbonpartiklernes overflade.

2. Fremgangsmåde ifølge krav 1, hvor substratmaterialet er kønrøg, aktiveret carbon, pyrolytisk carbon, graphit, et carbidafledt carbon, carbon-nanorør, graphen, et mesoporøst carbon, et nitrogendoteret og/eller bordoteret carbon eller en blanding af mindst to af disse carbonmaterialer, og/eller hvor platinforbindelsen er en platin(II)-forbindelse eller en platin(IV)-forbindelse.

3. Fremgangsmåde ifølge enten krav 1 eller krav 2, hvor imprægneringen af substratmaterialet udføres ved en pH-værdi for det vandige medium på ≤ 6.

4. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor reduktionsmidlet i trin (ii) er myresyre, et metalborhydrid, et alkalimetalhydrid, hydrogen, et metalthiosulfat, et aldehyd, hydrazin, hydrazinhydrat, hydrazinhydrochlorid eller ascorbinsyre eller en blanding af mindst to af disse reduktionsmidler.

5. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor omrører-Reynoldstallet i trin (ii) er i området på 75.000-180.000, og/eller pH-værdien for det vandige medium i trin (ii) er i området på 4,5-5,6.

6. Fremgangsmåde ifølge et hvilket som helst af de foregående krav, hvor det vandige medium i trin (ii) har en temperatur T i området på fra 20 °C til 95 °C.

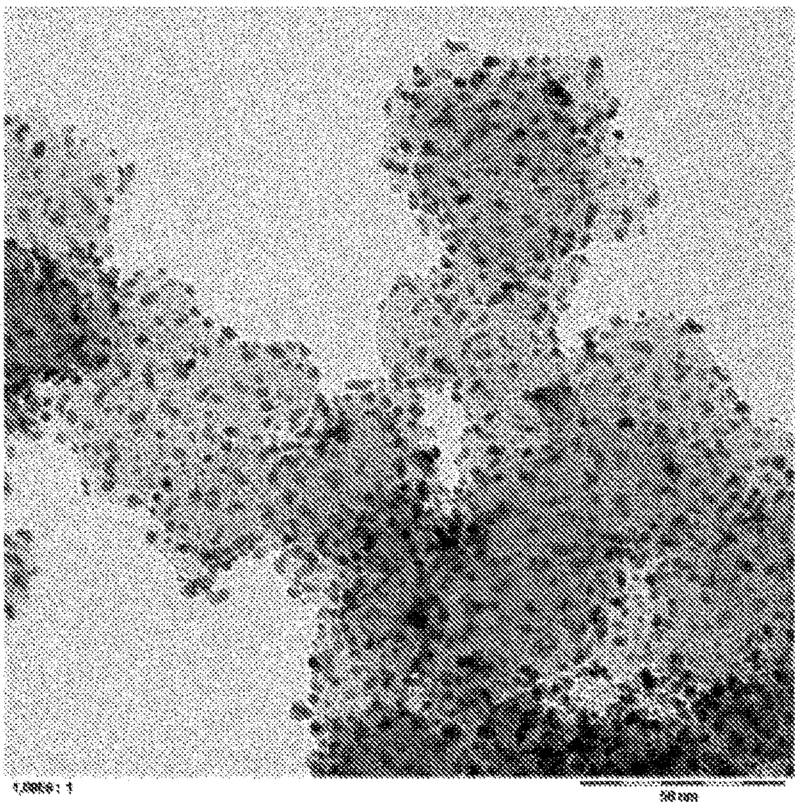

Figure 1

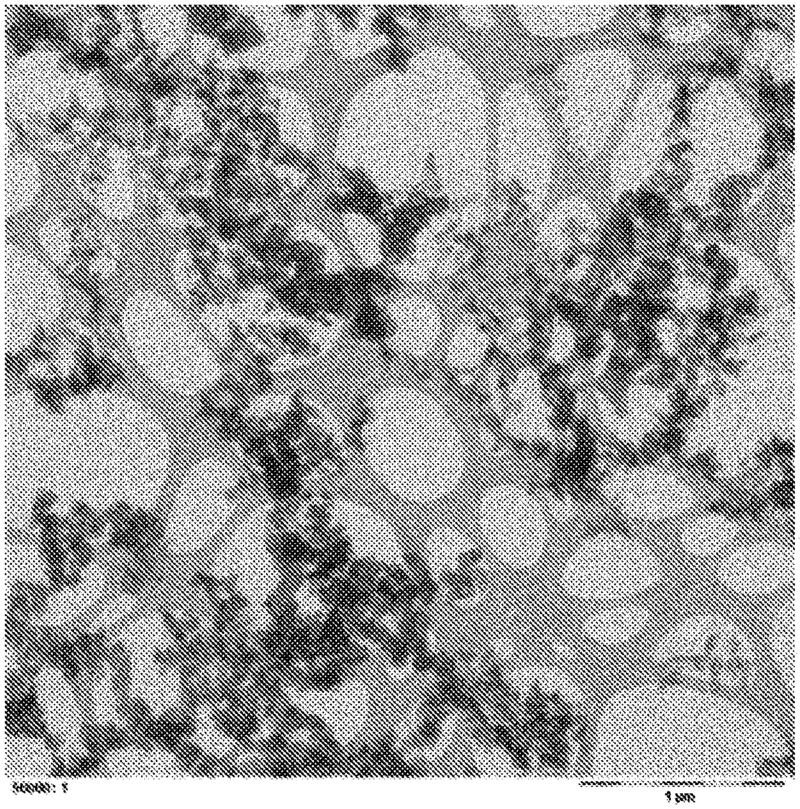

Figure 2

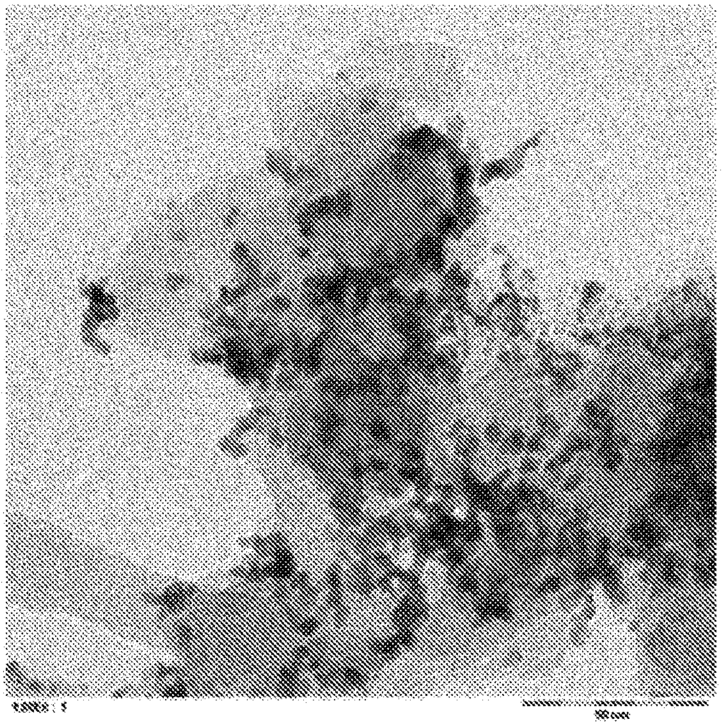

Figure 3

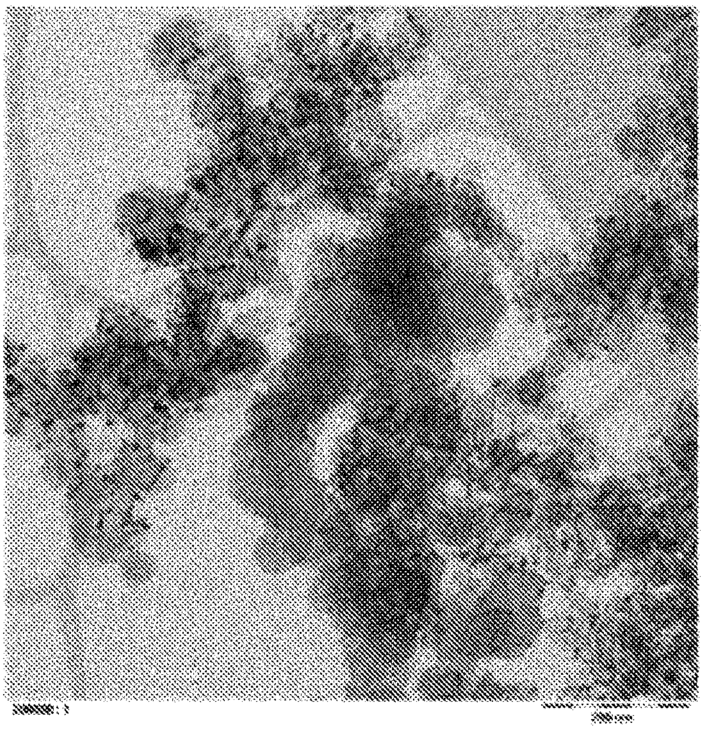

Figure 4

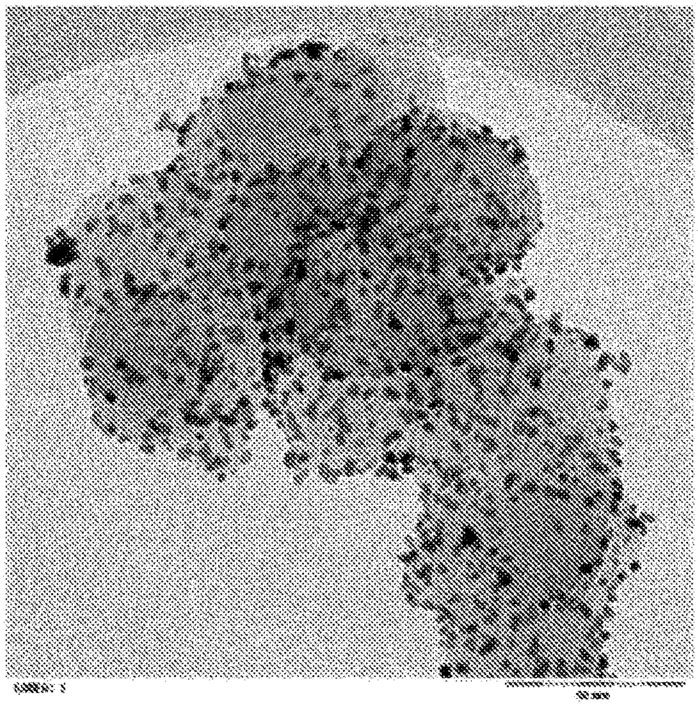

Figure 5

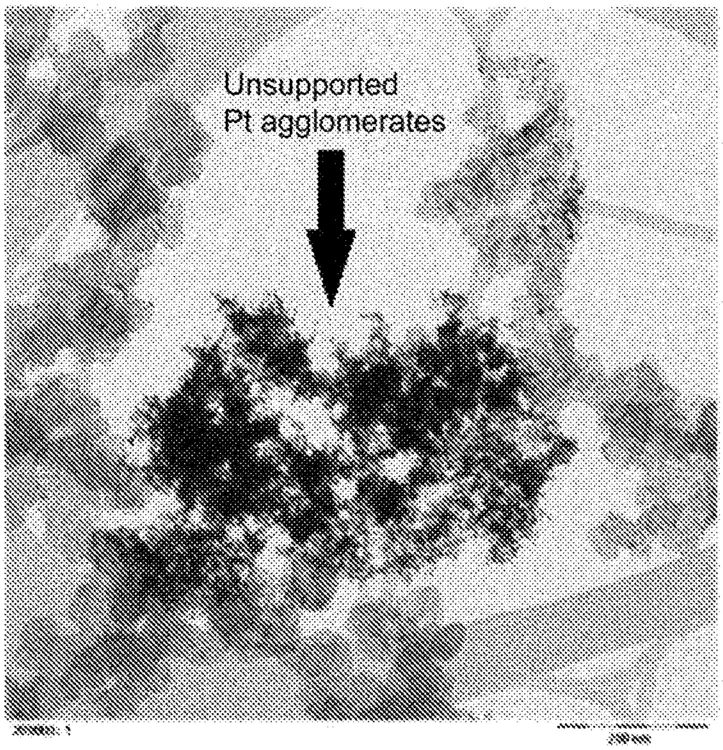

Figure 6