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(54) **CONDUCTIVE CATALYTIC PARTICLE AND METHOD OF PRODUCING CONDUCTIVE CATALYTIC PARTICLES**

(57) Conductive catalytic particle for heterogeneous catalysis as well as a method of producing said particles is presented. The method comprises a provision step (S1) of providing, in a vessel, porous particles comprising a porous support material carrying a catalyst material, and an impregnation step (S5) of exposing, in the vessel, the porous particles to an impregnation solution comprising a conductive polymer in carbon dioxide, thereby impregnating the porous particles with the conductive polymer to obtain the conductive catalytic particles.

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CONDUCTIVE CATALYTIC PARTICLE AND METHOD OF PRODUCING CONDUCTIVE CATALYTIC PARTICLES

The present disclosure relates to the technical field of conductive catalytic particles for heterogenous catalysis and methods of producing such particles.

Catalytic particles are used in a wide range of heterogeneous catalysis applications. Electrical conductivity of the catalytic particles is of importance in various electrochemical applications, such as electrolysis and fuel cells. Conductive catalytic particles are known for such applications. However, there is a need to improve existing technologies to ensure more sustainable processes.

The present disclosure provides improved conductive catalytic particles and methods of producing these, in particular regarding catalytic efficiency.

An aspect of the disclosure provides a method of producing conductive catalytic particles for heterogeneous catalysis. The method comprises a provision step of providing, in a vessel, porous particles comprising a porous support material carrying a catalyst material; and an impregnation step of exposing, in the vessel, the porous particles to an impregnation solution comprising a conductive polymer in carbon dioxide, thereby impregnating the porous particles with the conductive polymer to obtain the conductive catalytic particles.

This method offers a relatively uncomplicated method to produce conductive catalytic particles from various porous particles which comprise a porous support material carrying a catalyst material. Various materials are suitable for the porous support material and the catalyst material. It is therefore a versatile method.

The impregnation step may comprise controlling temperature and pressure in the vessel to have the carbon dioxide of the impregnation solution in a liquid or supercritical state. In other words, the impregnation step may be performed with liquid or supercritical carbon dioxide. Preferably, the carbon dioxide of the impregnation solution is in the supercritical state for the impregnation step. For example, a solution of the conductive polymer can be pumped into the vessel while the carbon dioxide is in liquid form, to be brought in the supercritical state once in the vessel by increasing temperature and/or pressure. In addition to the carbon dioxide of the impregnation solution, the impregnation solution as a whole may be in a liquid or supercritical state, when pumped into the vessel.

The method may further comprise a drying step of drying the obtained conductive catalytic particles. The drying step thus follows the impregnation step. The drying step serves to release the carbon dioxide and any co-solvent from the vessel and can be implemented in various ways, for example by purging and/or by depressurizing the vessel.

The provision step may comprise a synthesis step of providing the porous support material in the vessel and exposing the porous support material in the vessel to a catalyst impregnation solution, preferably comprising the catalyst material in carbon dioxide, thereby producing the porous particles comprising the porous support material carrying the catalyst material. Though it is preferred that the porous particles are synthesized in the same vessel also used for the impregnation step, the porous particles may also be synthesized in another vessel before being transferred into the vessel in which the impregnation step is performed. The porous particles carrying a catalyst material may be readily available at the start of the method. For example, commercially available catalysts in the form of porous particles can be improved with the method, in particular the impregnation step, as presently disclosed.

The synthesis step may comprise controlling temperature and pressure in the vessel to have the carbon dioxide of the catalyst impregnation solution in a liquid or supercritical state. The carbon dioxide may thus be liquid or supercritical in both the impregnation step as well as the synthesis step. It is preferred that the carbon dioxide is supercritical in at least one of these two steps, or even in both of these steps. As both the synthesis step and the impregnation step can be performed using carbon dioxide in liquid or supercritical state, and preferably in supercritical state, both the synthesis step and the impregnation step can be performed in the same vessel, thus providing a single reactor (vessel) method in the manufacture of conductive catalytic particles for heterogeneous catalysis.

The provision step may comprise an activation step of activating the catalyst material carried by the porous support material in the porous particles. The activation step may comprise calcination or reduction of the catalyst material carried by the porous support material in the porous particles. Activation, such as by calcination or reduction, may improve the catalytic activity of the catalyst material with respect to a particular reaction that is to be performed by the conductive catalytic particles. Examples include water splitting and fuel cell reactions.

Heterogeneous catalysts are typically supported, which means that the catalytic material is dispersed in, on and/or through the porous support material. Supports prevent or minimize

agglomeration and sintering of small catalyst particles and thus exposing more surface area, resulting in an increased specific activity of the catalytic material carried by the porous support compared to the catalytic material without the porous support. Various materials can be employed for the porous support material. The porous support material may be formed from a porous carbon, preferably in the form of activated carbon or graphene. Further, the porous support material may be formed from a porous metal oxide, preferably, but not limited to, selected from a group comprising silica, alumina, zinc oxide and cerium oxide. Said porous metal oxides may comprise silicon, aluminium, zinc, tin, cerium, one or more transition metals such as titanium and zirconium, or combinations thereof. Finally, the porous support material may be formed from a porous inorganic material.

The choice of catalyst material, just like the choice of porous support material, is not critical to the method. The catalyst material may be a metal-based catalyst, for example comprising Pt, Pd or Ni.

As for the conductive polymer, the term is meant to refer to intrinsically conductive polymers, which are organic polymers that conduct electric charge, for example in the form of electrons, protons, hydroxide or other ions. It includes polyelectrolytes, ionenes and ionomers.

It is preferred that the conductive polymer is an ionomer, which may in particular be selected from Anion Exchange Ionomers (AEIs) or Cation Exchange Ionomers (CEIs) typically used in the manufacture of membrane separators in electrochemical cells. The ionomer may for example be a sulfonated tetrafluoroethylene based fluoropolymer-copolymer or a sulfonated poly-styrene based material. Examples of current state-of-the-art AEIs are the benzyltrimethylammonium-functionalized poly(ethylene-co-tetrafluoroethylene) (BTMA-ETFE) ionomers, polyfluorene (FLN) ionomers, poly(terphenyl piperidinium) (PTP) ionomers, poly(biphenyl piperidinium) (PBP) ionomers. An example of a current state-of-the-art CEI is perfluorosulfonic-acid (PFSA).

The composition of the impregnation solution may be chosen based on the conductive polymer to be impregnated into the porous particles. The impregnation solution may further comprise a co-solvent miscible with the conductive polymer and carbon dioxide under process operating conditions in the vessel. A co-solvent may improve solubility of the conductive polymer in liquid or supercritical carbon dioxide. The type and quantity of a co-solvent are generally selected depending on conductive polymer and reaction conditions. Examples of relevant cosolvents include water and alcohols, preferably a C1, C2 or C3 alcohol such as methanol, ethanol and iso-propanol.

The method advantageously allows the same vessel to be used for its various steps. A single vessel suffices to produce conductive catalytic particles merely requiring, in the simplest form of the method, the porous particles, the conductive polymer and carbon dioxide. Synthesis of the porous particles can be performed in the same vessel using, as a minimum, the porous material and the catalyst material in addition to the aforementioned material. The same source of carbon dioxide can be used for both the synthesis step and the impregnation step.

Another aspect of the disclosure provides a conductive catalytic particle for heterogeneous catalysis, obtainable by the methods as disclosed herein.

Conductive catalytic particles obtained by the method, in particular via the impregnation step thereof, exhibit improved characteristics, for example in relation to electrical conductivity and/or increased catalytic performance compared to conductive catalytic particles produced using a conventional method of impregnations (such as by sonication).

The inventors have also observed improvements in shape, morphology and/or size of the conductive catalytic particles obtained by the method, which are more rounded and/or more monodisperse than can be obtained by impregnation based on conventional sonication techniques.

The conductive catalytic particle may comprise a porous support material, a catalyst material and a conductive polymer. The catalyst material is in particular carried by the porous support material and the conductive polymer is impregnated into the porous particle formed by the porous support material carrying the catalyst material.

The porous support material, the catalyst material and the conductive polymer can be formed of any of the materials given above.

The conductive catalytic particle as disclosed herein may be characterized by various parameters, including the following.

The conductive catalytic particle may have a cross-sectional size in the range of from 0.1 μm to $1 \cdot 10^2$ μm, preferably from 1 μm to $1 \cdot 10^2$ μm, more preferably from 1 μm to 50 μm, as measured by electron microscopy. In particular, scanning electron microscopy or transmission electron microscopy can be employed.

The conductive catalytic particle may have a cross-section with a roundness in the range of from 0.3 to 1, preferably from 0.5 to 1, more preferably from 0.7 to 1. The definition of roundness used herein is the ratio of the radii of inscribed and circumscribed circles of the shape under consideration. The inscribed radius and circumscribed radius refer to the maximum and minimum sizes for circles that are just sufficient to fit inside or to enclose the cross-sectional shape of the particle, respectively. This is also known as the ISO definition of roundness and ranges from 0 (not round at all) to 1 (shape of a circle). Roundness is computed as r / R with r being the inscribed radius and R being the circumscribed radius of the shape under consideration as measured by electron microscopy.

Another aspect of the disclosure provides a catalytic formulation comprising conductive catalytic particles as disclosed herein. The catalytic formulation may further include a liquid phase in addition to a particulate phase formed by the conductive catalytic particles. The liquid phase may be formulated for the intended use of the catalytic formulation and may include (remnants of) the co-solvent used in the impregnation step. The catalytic formulation may be a catalytic ink, in particular suitable for coating onto membranes for electrochemical cells to obtain what are known as catalyst-coated membranes (CCM).

Another aspect of the disclosure provides catalyst-coated membranes comprising a membrane having at least one face provided with conductive catalytic particles as disclosed herein. The catalyst-coated membranes can be obtained by the application of the conductive catalytic particles obtained using the methods of the invention onto a membrane, in particular a ceramic or a polymer membrane, using a catalytic formulation as disclosed herein, e.g. in the form of a catalytic ink. Techniques to apply such catalytic ink include ink-jetting, sputtering, spin-coating and the like. Conductive catalytic particles of a first type may be coated on a first face of the membrane, while conductive catalytic particles of a second type may be coated on a second face of the membrane. In other words, both sides of the membrane may be coated with different conductive catalytic particles.

No separate binder is needed to couple the conductive catalytic particles to the surface of the membrane, as the conductive polymer, in particular in the form of an ionomer, performs the function of binder.

In a particular aspect the catalyst-coated membrane may have a membrane that is formed with a conductive polymer corresponding to the conductive polymer of the conductive catalytic particle. Here, the term corresponding refers to the conductive polymers being identical, but may also mean

that these have at least common monomers, common blocks of co-polymers, or common side chains. In said instance where the membrane is formed with a conductive polymer corresponding to the conductive polymer of the conductive catalytic particle, the binding of the conductive catalytic particles to the surface of the membrane was found to be enhanced.

Another aspect of the disclosure provides an electrochemical cell comprising two electrodes separated by a catalyst-coated membrane as disclosed herein.

Improvements in electrochemical performance have been observed when the conductive catalytic particles obtained by the method are used to coat membranes of an electrochemical cell, in particular an electrolytic cell.

The electrochemical cell may be a fuel cell, an electrolytic cell or an electrolyzer, for example.

A final aspect of the disclosure presents uses of the conductive catalytic particles as disclosed herein in the manufacturing of a heterogeneous catalytic material, a catalytic formulation, a catalytic ink, a catalyst-coated membrane and/or an electrochemical cell.

The description following below with the associated figures further address aspects of the present disclosure. In the figures:

FIG. 1	shows a schematic illustration of a catalyst particle;
FIG. 2	shows a schematic illustration of an electrochemical cell with a catalyst-coated membrane;
FIGS. 3A-3B	show electron microscopy images of conductive catalytic particles obtained by a method according to a comparative example (FIG. 3A) and by a method according to the present disclosure (FIG. 3B), respectively;
FIGS. 4A-4B	show particle size distribution diagrams of the particles imaged in FIGS. 3A-3B;
FIG. 5	shows electrochemical test results of the particles imaged in FIGS. 3A-3B;
FIG. 6	shows a reactor design for producing conductive catalytic particles; and
FIG. 7	shows a flow diagram of a method of producing conductive catalytic particles.

The following reference signs are used:

10	conductive catalytic particle
11	porous support material
12	catalyst material
13	porous particle

14	conductive polymer
20	catalyst-coated membrane
21	polymer membrane layer
22	first face of membrane
23	second face of membrane
24	first catalyst coating, composition or ink
25	second catalyst coating, composition or ink
30	electrochemical cell
31	first half-cell
32	second half-cell
33	first connection (e.g. cathode)
34	second connection (e.g. anode)
35	power source (e.g. voltage supply)
40	reactor
41	vessel
42	openable cover
43	stirrer
44	vanes
45	drive
46	infeed
47	outlet
S1	provision step
S2	synthesis step
S3	purging step
S4	activation step
S5	impregnation step
S6	drying step

In FIG. 1, a schematic and even cartoon-like illustration of a conductive catalytic particle 10 is shown. It shows a porous support material 11 with therein a distribution of catalyst material 12. The dark lines represent a well-distributed network of conductive polymer 13 within the conductive catalytic particle. Notable in this cartoon-like presentation of a conductive catalytic particle 10 according to the invention is its overall round (sphere like) shape, shown to be a result of the impregnation method according to the invention, and found to improve the catalyst activity of the thus obtained materials (see Figure 5 below).

The conductive catalytic particles may find use in various applications. An example is shown in FIG. 2, which presents a schematic illustration of an electrochemical cell 30 comprising a catalyst coated membrane 20 obtained by applying a catalytic formulation (ink) 24, 25 comprising conductive catalytic particles 10 as herein disclosed at either face 22, 23 of a polymer membrane 21. As mentioned before, the catalytic formulation at either side of the membrane could be the same or different, that is in particular the same or different in relation to the conductive catalytic particles 10 present in said catalytic formulations. Each side of the membrane corresponds to the catalytic phase of a respective first 31 and second 32 half-cell of the electrochemical cell, with in the shown cell 30 at the cathode side 33 the formation of hydrogen (H_2) and at the anode side 34 the formation of oxygen (O_2) from water (H_2O) fed into the cell via the polymer membrane 21, when an electrical power source 35 (e.g. voltage) is being applied. It is noted that the catalyst-coated membrane 20 may also be provided with a catalyst coating on only one of its faces 22, 23.

FIGS. 3A-3B show electron microscopy images of conductive catalytic particles obtained by a method according to a comparative example and by a method according to the present disclosure, respectively. In the comparative example the same porous support material carrying a catalyst material is impregnated with an impregnation solution comprising the same conductive polymer, by means of sonication instead of the carbon dioxide-based impregnation step of the present invention. The electron microscopy images clearly show a difference in the morphology of the conductive catalytic particles. Note the difference in scale. With the impregnation by sonication (Figure 3A) larger particles are obtained, and these particles are irregular in shape. This in contrast to the impregnation by means of liquid or super-critical carbon dioxide, resulting in smaller and more spherically shaped particles. Image analysis of FIG. 3B provides roundness values in the range of 0.7 – 0.9. Therefore, and using the method of the present invention the active surface area of the conductive catalytic particles is significantly increased.

To underscore the above, FIGS. 4A-4B show particle size distribution diagrams of the particles imaged in FIGS. 3A-3B. It nicely confirms the visual observation of the electron microscopy images with a narrower size distribution for the conductive catalytic particles obtained by the method of the invention. Compared to the impregnation by sonication, the particles of the invention have an average particle size in the single digit μm size, in particular from about 2 to about 6 μm.

FIG. 5 shows comparative electrochemical test results of the particles imaged in FIGS. 3A-3B. The voltage vs. current density graph presents the reduction of electrolysis cell potential for the catalyst particles obtained according to invention when compared to conventional particles. This is

advantageous because a lower voltage is needed to obtain the same current density for electrolysis to take place (i.e. the catalyst of the invention makes the system more efficient). Expressed differently, given the higher active surface area the conductive catalytic particles obtained by a method according to the invention are more efficient in their catalytic activity.

FIG. 6 shows a reactor 40 design for producing conductive catalytic particles with the method as herein provided. In its simplest form, the reactor consists of a vessel 41, comprising stirring means, here represented by a stirrer 43 with drive means (motor) 45 and vanes 44. The method being performed in the presence of liquid and preferable supercritical carbon dioxide, the reactor vessel 41 needs to be closed, preferably with an openable cover 42, enabling pressurizing of the reactor vessel when fed via an inlet 46 with the impregnation solution and/or catalyst impregnation solution. Outlet 47 enables venting of the carbon dioxide (CO_2) and eventual co-solvents at the end of the procedure or between process steps where needed. At the start, the vessel 41 is filled with non-conductive catalytic particles. The vessel is closed, fed with the impregnation solution comprising liquid carbon dioxide (CO_2) and the conductive polymer 14, optionally in the presence of a co-solvent. The pressure and temperature in the vessel are controlled such that at least the carbon dioxide (CO_2), and preferably the whole impregnation solution is in a supercritical phase. Stirring the non-conductive catalytic particles in such environment results in the impregnation of the particles with the conductive polymer, yielding the conductive catalytic particles 10 according to the invention.

FIG. 7 shows a flow diagram of a method of producing conductive catalytic particles.

The provision step S1 includes at least the provision of a porous support material carrying a catalyst material into the reactor. As mentioned, the impregnation step can be performed on existing porous support material carrying a catalyst material, in converting such materials into conductive catalytic materials. Alternatively, the provision step includes the actual synthesis of such porous support material carrying a catalyst material, starting from a porous support 11.

In such instance the provision step S1 includes a synthesis step S2 wherein a porous support 11 is fed into the reactor and said material is impregnated with a catalyst impregnation solution. As for the impregnation step S2, this is preferably performed with a catalyst impregnation solution comprising liquid carbon dioxide, wherein the pressure and temperature in the vessel are controlled such that at least the carbon dioxide, and preferably the whole catalyst impregnation solution, is in a supercritical phase. Stirring the porous support particles 11 in such environment results in the impregnation of the particles with the catalyst 12, yielding a porous support material carrying a

catalyst material. After purging S3 the reactor to vent the carbon dioxide, the porous support material carrying a catalyst material may undergo a subsequent activation step S4 with a final purging S3.

In order to obtain the conductive catalytic particles 10 according to the invention, the method includes an impregnation step S5 in the reactor of the porous support material carrying a catalyst material provided or obtained in provision step S1, using an impregnation solution comprising liquid carbon dioxide and the conductive polymer 14, optionally in the presence of a co-solvent. During the impregnation step S5, the pressure and temperature in the vessel are controlled such that at least the carbon dioxide, and preferably the whole impregnation solution, is in a supercritical phase. Stirring the non-conductive catalytic particles in such environment results in the impregnation of the particles with the conductive polymer, yielding after drying (step S6) the conductive catalytic particles 10 according to the invention.

As evident from the foregoing, the purging step S3 includes purging the vessel and may be performed at various stages of the method. For example, purging steps S3 may be performed between the synthesis step S2 and the activation step S4, and/or between the activation step S4 and the impregnation step S5. The drying step S6 may also involve purging, e.g. include a purging step S3.

EXAMPLE

The following presents an exemplary implementation of the method.

Synthesis step S1

Step S2 & S3. Metal salt impregnation of porous support

a. Mix metal salt and porous support in the high-pressure reactor
b. Purge reactor from air by passing CO_2 at 2 – 3 bar for few minutes
c. Increase pressure and temperature (up to 200 bar and 200°C)
d. Keep for at least 12 – 24h
e. Depressurize and reduce temperature

Step S4 & S3. Activation of the metal salt impregnated porous support

a. Including heat treatment (calcination) and/or subsequent hydrogen gas treatment (reduction), depending on the oxidation state needed for the active phase (catalyst) with respect to the desired reaction to occur.

a1. If calcination is needed, the reactor is heated to between 200 – 300°C (higher might be needed depending on the catalyst, e.g. metal), under the flow of a noble gas or flowing or static air depending on the recipe, for 5 – 10 h.

a2. If reduction is needed, the reactor is under flow of hydrogen gas at a temperature between 100 – 300°C for 2 – 4h.

b. Purge under a noble gas (such as helium) to remove byproduct

For example, the purging step S3 between the synthesis step S2 and the activation step S4 or between the activation step S4 and the impregnation step S5 may involve purging the vessel with carbon dioxide for a few minutes under 2 – 5 bar

Impregnation step S5

Phase diagrams are available to determine the conditions in which carbon dioxide is in a liquid or supercritical state. For example, carbon dioxide may be in a supercritical state at a temperature of at least 31 °C and pressure of at least 7.4 MPa. The impregnation step S5 may involve having the carbon dioxide in a liquid state, for example by pressurizing the vessel to 20 – 150 bar at a temperature of 5 – 30°C (i.e. below the critical temperature).

The reactor vessel is kept under pressure and temperature control for 6 – 10 h. The composition inside the vessel may be stirred during this time.

When the vessel has a viewing window, the liquid or supercritical state of at least the carbon dioxide can be observed visually. Carbon dioxide in supercritical state has a foggy appearance.

Drying step S6

The vessel may be depressurized to commence drying the produced conductive catalytic particles. Carbon dioxide is allowed to evaporate, via the outlet 47 and/or by opening the openable cover 42 of the reactor 40.

Drying may also include evaporation of any co-solvents e.g. small molecule alcohols as listed above and/or water). However, co-solvents may also remain, to provide a catalytic formulation that could, for example, be employed as a catalytic ink.

CONCLUSIES

1. Een werkwijze van het produceren van geleidende katalytische deeltjes voor heterogene katalyse, omvattende:
   - een verschaffingsstap (S1) van het in een vat verschaffen van poreuze deeltjes omvattende een poreus dragermateriaal dat een katalysatormateriaal draagt; en
   - een impregnatiestap (S5) van het in het vat blootstellen van de poreuze deeltjes aan een impregnatieoplossing omvattende een geleidend polymeer in koolstofdioxide, waardoor de poreuze deeltjes met het geleidende polymeer worden geïmpregneerd om de geleidende katalytische deeltjes te verkrijgen.

2. Werkwijze van conclusie 1, waarbij de impregnatiestap (S5) het beheersen van temperatuur en druk in het vat omvat om het koolstofdioxide van de impregnatieoplossing in een vloeibare of superkritische toestand te hebben.

3. Werkwijze van conclusie 1 of 2, verder omvattende een droogstap (S6) van het drogen van de verkregen geleidende katalytische deeltjes.

4. Werkwijze van een willekeurige voorgaande conclusie, waarbij de verschaffingsstap (S1) een synthesestap (S2) omvat van het in het vat verschaffen van het poreuze dragermateriaal en het in het vat blootstellen van het poreuze dragermateriaal aan een katalysatorimpregnatieoplossing omvattende het katalysatormateriaal in koolstofdioxide, waardoor de poreuze deeltjes omvattende het poreuze dragermateriaal dat het katalysatormateriaal draagt worden geproduceerd.

5. Werkwijze van conclusie 4, waarbij de synthesestap (S2) het beheersen van temperatuur en druk in het vat omvat om het koolstofdioxide van de katalysatorimpregnatieoplossing in een vloeibare of superkritische toestand te hebben.

6. Werkwijze van een willekeurige voorgaande conclusie, waarbij de verschaffingsstap (S1) een activatiestap (S4) omvat van het activeren van het katalysatormateriaal dat door het poreuze dragermateriaal in de poreuze deeltjes wordt gedragen.

7. Werkwijze van conclusie 6, waarbij de activatiestap (S4) calcinatie of reductie omvat van het katalysatormateriaal dat door het poreuze dragermateriaal in de poreuze deeltjes wordt gedragen.

8. Werkwijze van een willekeurige voorgaande conclusie, waarbij het poreuze dragermateriaal is gevormd van een poreus koolstof, bij voorkeur in de vorm van geactiveerd koolstof of grafeen, of een poreus metaaloxide, bij voorkeur geselecteerd uit oxides omvattende silicium, aluminium, zink, tin, cerium, één of meer overgangsmetalen zoals titanium en zirkonium, of combinaties daarvan, of een poreus anorganisch materiaal.

9. Werkwijze van een willekeurige voorgaande conclusie, waarbij het katalysatormateriaal een op metaal gebaseerde katalysator is, bij voorkeur omvattende Pt, Pd of Ni.

10. Werkwijze van een willekeurige voorgaande conclusie, waarbij het geleidende polymeer een ionomeer is, in het bijzonder geselecteerd uit anionen uitwisselende ionomeren of kationen uitwisselende ionomeren die typisch worden gebruikt bij het produceren van membraanscheidingen voor elektrochemische cellen.

11. Geleidend katalytische deeltje voor heterogene katalyse, verkrijgbaar met de werkwijze volgens een willekeurige van de conclusies 1 – 10.

12. Geleidend katalytische deeltje van conclusie 11, omvattende een poreus dragermateriaal, een katalysatormateriaal en een geleidend polymeer.

13. Geleidend katalytische deeltje van conclusie 11 of 12, waarbij het poreus dragermateriaal is gevormd uit een poreuze koolstof, bij voorkeur in de form van geactiveerde koolstof of grafeen, of een poreuze metaaloxide, bij voorkeur geselecteerd uit een groep omvattende silica, alumina, zinkoxide en ceriumoxide, of een poreus anorganisch materiaal.

14. Geleidend katalytische deeltje van een willekeurige van de conclusies 11 tot en met 13, waarbij het katalysatormateriaal een op metaal gebaseerde katalysator is, bij voorkeur omvattende Pt, Pd of Ni.

15. Geleidend katalytische deeltje van een willekeurige van de conclusies 11 tot en met 14, waarbij de geleidende polymeer een ionomeer is, in het bijzonder geselecteerd uit anionen uitwisselende ionomeren of kationen uitwisselende ionomeren die typisch worden gebruikt bij het produceren van membraanscheidingen voor elektrochemische cellen.

16. Geleidend katalytische deeltje van een willekeurige van de conclusies 11 tot en met 15, met een grootte in dwarsdoorsnede in het bereik vanaf 0.1 µm tot en met $1 \cdot 10^2$ µm, bij voorkeur vanaf 1 µm tot en met $1 \cdot 10^2$ µm, meer bij voorkeur vanaf 1 µm tot en met 50 µm, zoals gemeten met elektronenmicroscopie.

17. Geleidend katalytisch deeltje van een willekeurige van de conclusies 11 tot en met 16, met een dwarsdoorsnede met een rondheid in het bereik vanaf 0.3 tot en met 1, bij voorkeur vanaf 0.5 tot en met 1, meer bij voorkeur vanaf 0.7 tot en met 1, waarbij rondheid is berekend als r / R waarbij r de ingeschreven cirkelstraal is en R de omgeschreven cirkelstraal is van de dwarsdoorsnede zoals gemeten met elektronenmicroscopie.

18. Katalytische formulering omvattende geleidende katalytische deeltjes volgens een willekeurige van de conclusies 11 tot en met 17.

19. Katalysator-gecoat membraan omvattende een membraan met ten minste één zijde voorzien van geleidende katalytische deeltjes van een willekeurige van de conclusies 11 tot en met 17 of de katalytisch formulering van conclusie 18.

20. Katalysator-gecoat membraan van conclusie 19, waarbij het membraan is gevormd met een geleidend polymeer dat correspondeert met het geleidende polymeer van het geleidende katalytische deeltje.

21. Elektrochemische cel omvattende twee elektrodes gescheiden door een katalysator-gecoat membraan volgens conclusie 19 of 20.

22. Elektrochemische cel van conclusie 21, waarbij de elektrochemische cel een brandstofcel, elektrolyseur of elektrolytische cel is.

23. Gebruik van geleidende katalytische deeltjes volgens een willekeurige van de conclusies 11 tot en met 17 bij het vervaardigen van een heterogeen katalytisch materiaal, een katalytische formulering, een katalytische inkt, een katalysator-gecoat membraan en/of een elektrochemische cel.

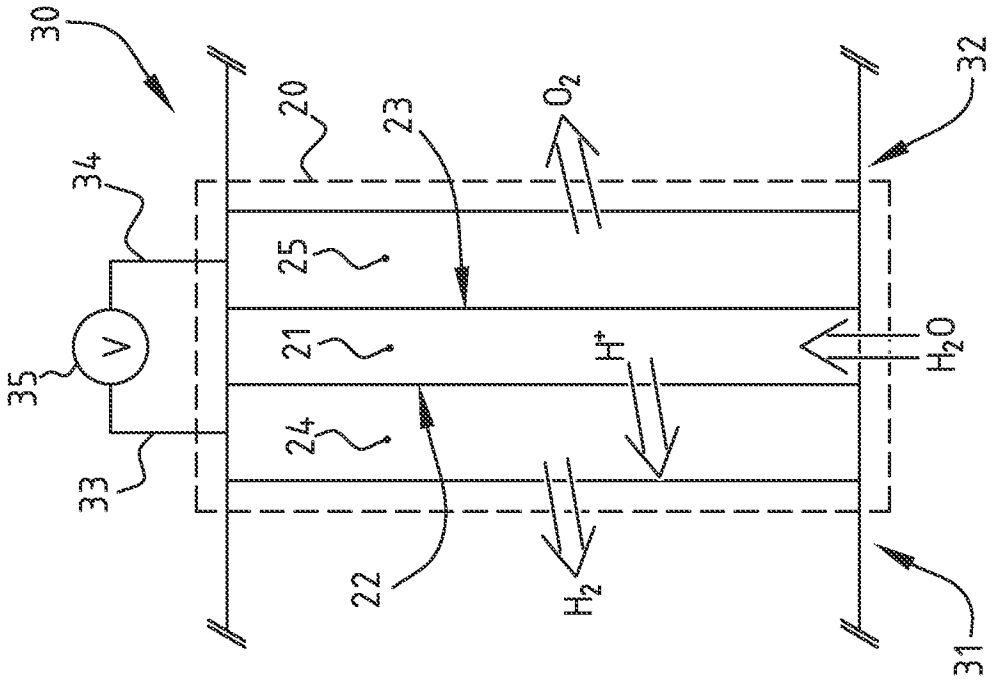

FIG. 2

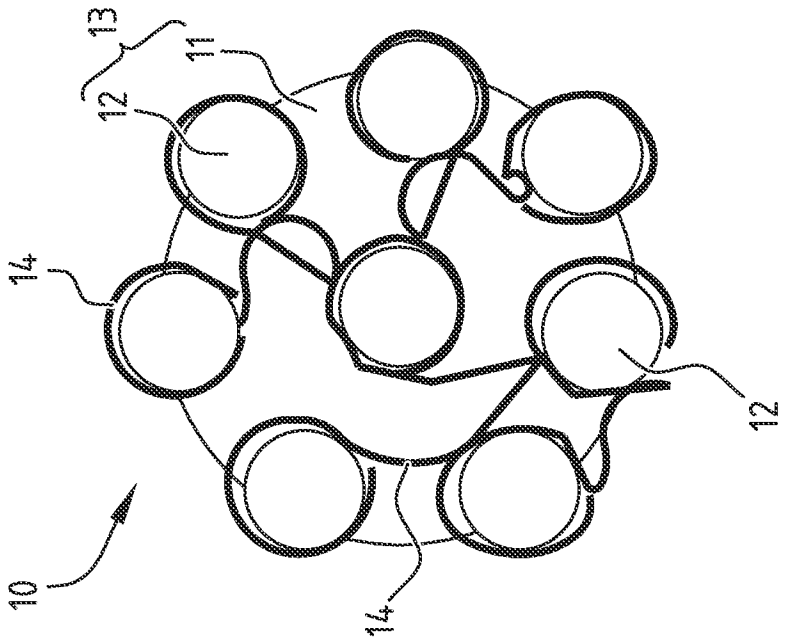

FIG. 1

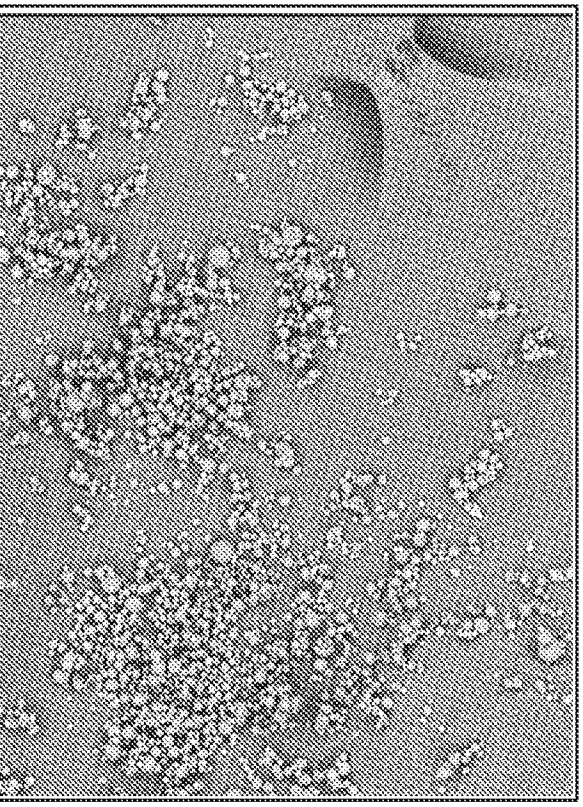

FIG. 3B

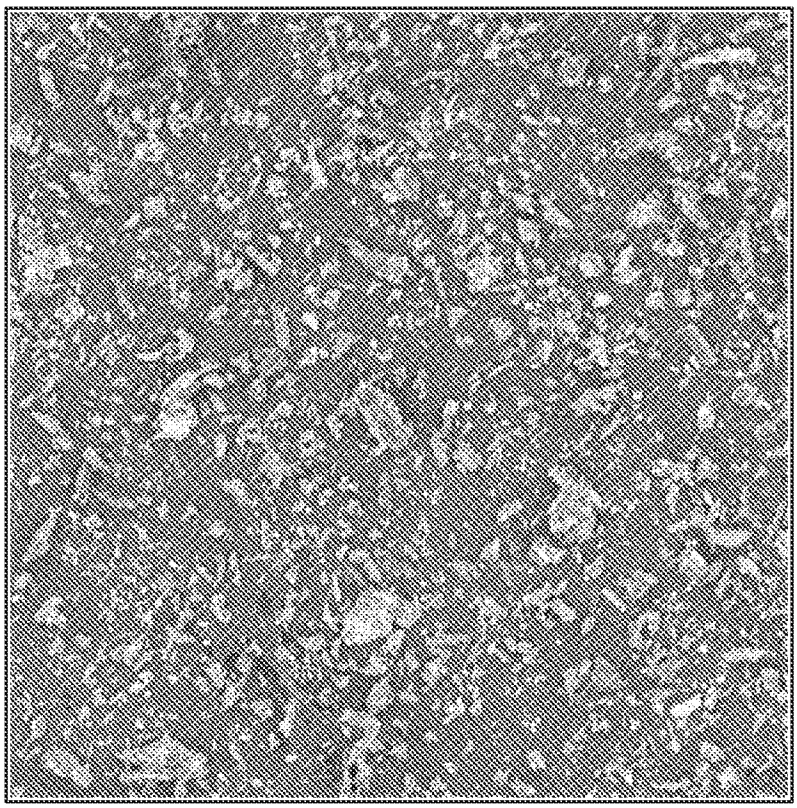

FIG. 3A

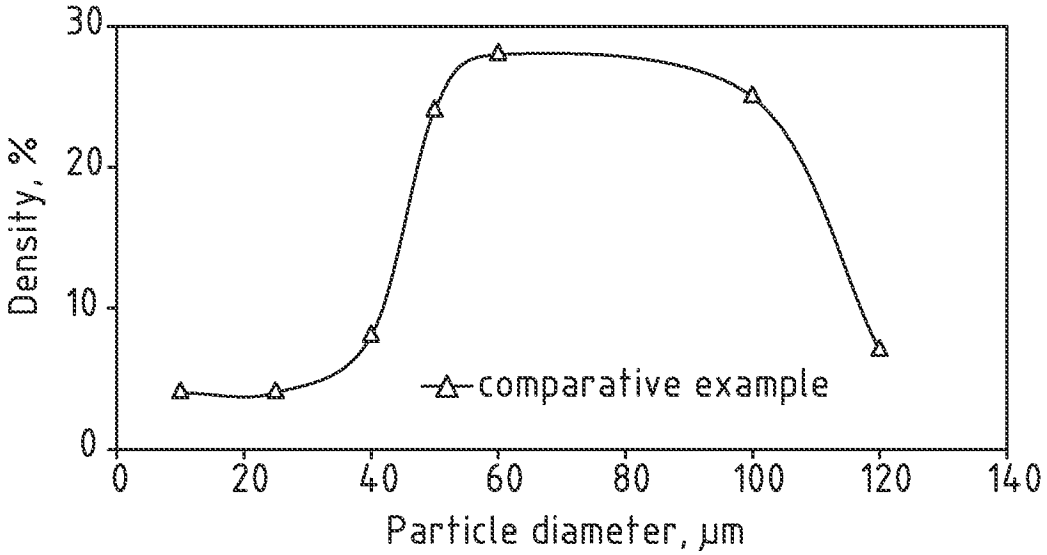
30
20
10
0
Density, %
comparative example
0
20
40
60
80
100
120
140
Particle diameter, μm

FIG. 4A

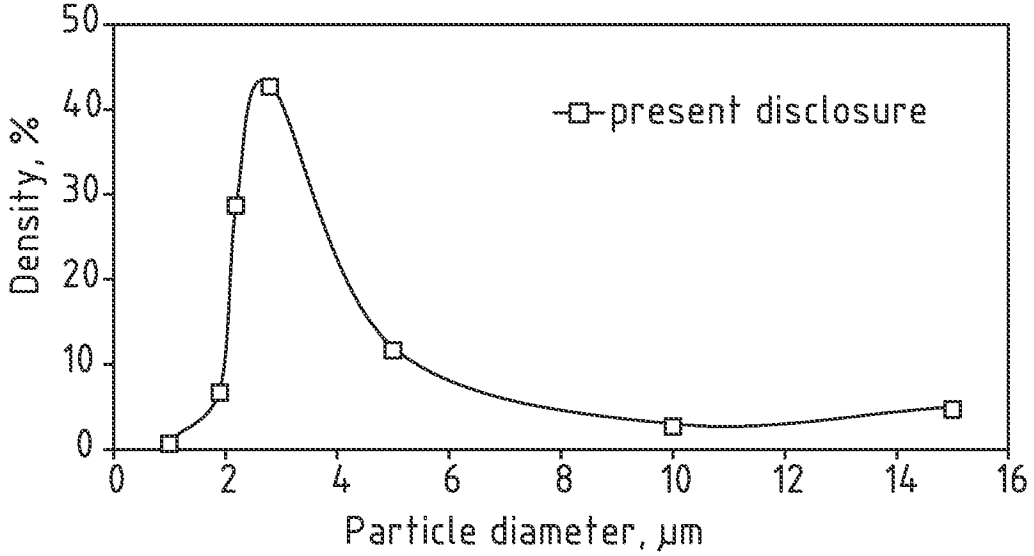
50
40
30
20
10
0
Density, %
present disclosure
0
2
4
6
8
10
12
14
16
Particle diameter, μm

FIG. 4B

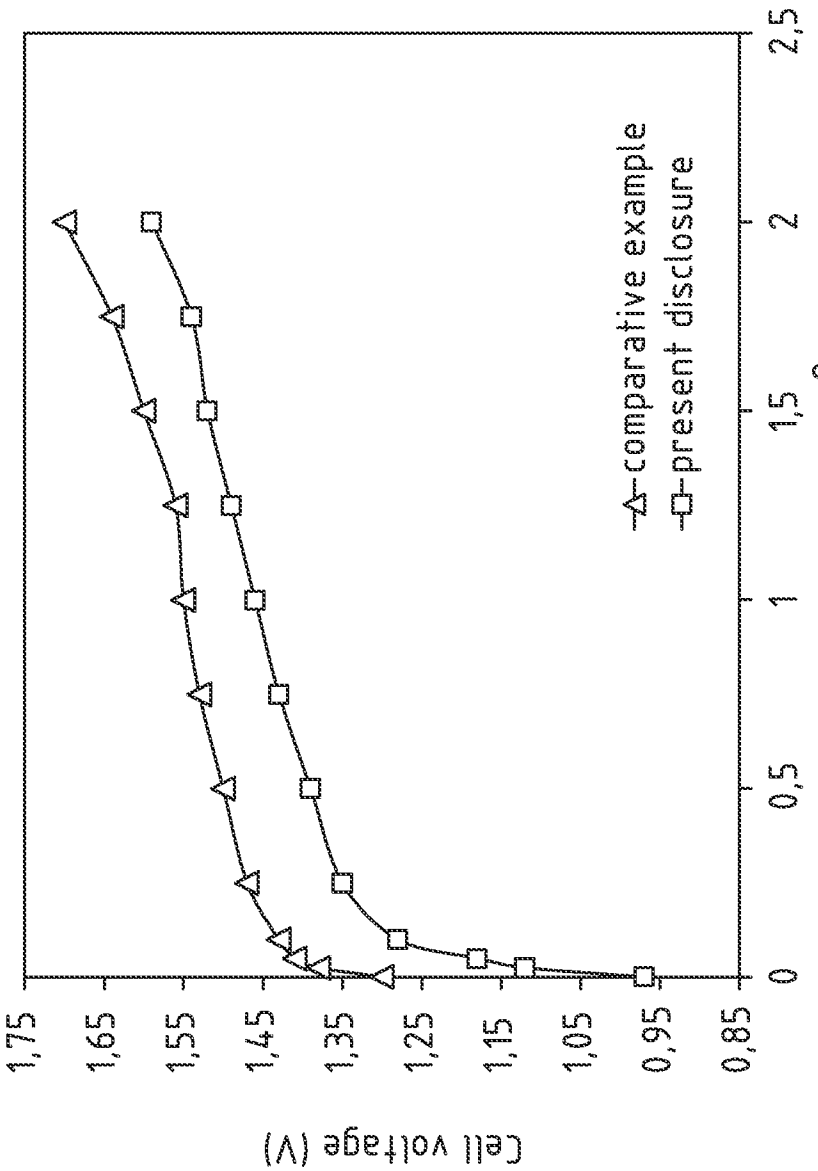
Cell voltage (V)
1,75
1,65
1,55
1,45
1,35
1,25
1,15
1,05
0,95
0,85
0
0,5
1
1,5
2
2,5
Current density (A cm-2)
comparative example
present disclosure

FIG. 5

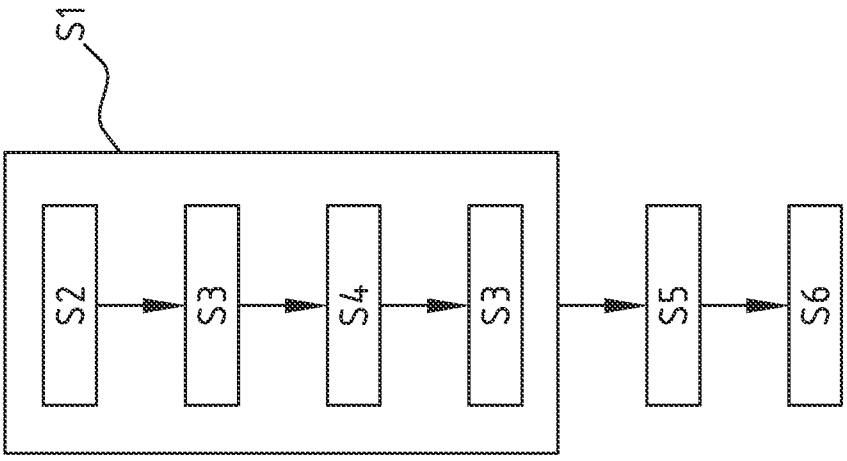

FIG. 7

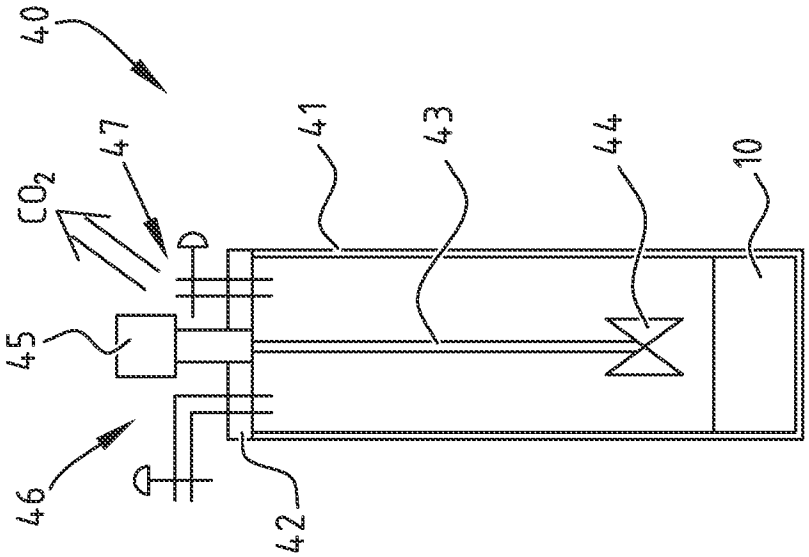

FIG. 6

SAMENWERKINGSVERDRAG (PCT)

RAPPORT BETREFFENDE NIEUWHEIDSONDERZOEK VAN INTERNATIONAAL TYPE

IDENTIFICATIE VAN DE NATIONALE AANVRAGE	KENMERK VAN DE AANVRAGER OF VAN DE GEMACHTIGDE
Nederlands aanvraag nr. **2034462**	Indieningsdatum **29-03-2023**
	Ingeroepen voorrangsdatum
Aanvrager (Naam) **Sotoodeh Beheer B.V.**	
Datum van het verzoek voor een onderzoek van internationaal type **24-06-2023**	Door de Instantie voor Internationaal Onderzoek aan het verzoek voor een onderzoek van internationaal type toegekend nr. **SN84107**

I. CLASSIFICATIE VAN HET ONDERWERP (bij toepassing van verschillende classificaties, alle classificatiesymbolen opgeven)

Volgens de internationale classificatie (IPC)

Zie onderzoeksrapport

II. ONDERZOCHTE GEBIEDEN VAN DE TECHNIEK

Onderzochte minimumdocumentatie

Classificatiesysteem	Classificatiesymbolen
IPC	**Zie onderzoeksrapport**

Onderzochte andere documentatie dan de minimum documentatie, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen

III.	☐	**GEEN ONDERZOEK MOGELIJK VOOR BEPAALDE CONCLUSIES**	(opmerkingen op aanvullingsblad)
IV.	☐	**GEBREK AAN EENHEID VAN UITVINDING**	(opmerkingen op aanvullingsblad)

ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Nummer van het verzoek om een onderzoek naar de stand van de techniek
NL 2034462

A. CLASSIFICATIE VAN HET ONDERWERP

INV. B01J37/02 B01J21/18 B01J23/40 B01J35/00 H01M4/86 H01M4/92

ADD.

Volgens de Internationale Classificatie van octrooien (IPC) of zowel volgens de nationale classificatie als volgens de IPC.

B. ONDERZOCHTE GEBIEDEN VAN DE TECHNIEK

Onderzochte miminum documentatie (classificatie gevolgd door classificatiesymbolen)

B01J H01M

Onderzochte andere documentatie dan de mimimum documentatie, voor dergelijke documenten, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen

Tijdens het onderzoek geraadpleegde elektronische gegevensbestanden (naam van de gegevensbestanden en, waar uitvoerbaar, gebruikte trefwoorden)

EPO-Internal, WPI Data

C. VAN BELANG GEACHTE DOCUMENTEN

Categorie °	Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.
X	JP 2010 027512 A (TOYOTA MOTOR CORP) 4 februari 2010 (2010-02-04)	11-23
A	* alineas [0020] - [0031] *	1-10
X	US 2005/200040 A1 (HARA HIROAKI S [US] ET AL) 15 september 2005 (2005-09-15) * alinea [0031]; figuur 2 *	11-23

☐ Verdere documenten worden vermeld in het vervolg van vak C.

☒ Leden van dezelfde octrooifamilie zijn vermeld in een bijlage

° Speciale categorieën van aangehaalde documenten

"A" niet tot de categorie X of Y behorende literatuur die de stand van de techniek beschrijft

"D" in de octrooiaanvrage vermeld

"E" eerdere octrooi(aanvrage), gepubliceerd op of na de indieningsdatum, waarin dezelfde uitvinding wordt beschreven

"L" om andere redenen vermelde literatuur

"O" niet-schriftelijke stand van de techniek

"P" tussen de voorrangsdatum en de indieningsdatum gepubliceerde literatuur

"T" na de indieningsdatum of de voorrangsdatum gepubliceerde literatuur die niet bezwarend is voor de octrooiaanvrage, maar wordt vermeld ter verheldering van de theorie of het principe dat ten grondslag ligt aan de uitvinding

"X" de conclusie wordt als niet nieuw of niet inventief beschouwd ten opzichte van deze literatuur

"Y" de conclusie wordt als niet inventief beschouwd ten opzichte van de combinatie van deze literatuur met andere geciteerde literatuur van dezelfde categorie, waarbij de combinatie voor de vakman voor de hand liggend wordt geacht

"&" lid van dezelfde octrooifamilie of overeenkomstige octrooipublicatie

Datum waarop het onderzoek naar de stand van de techniek van internationaal type werd voltooid	Verzenddatum van het rapport van het onderzoek naar de stand van de techniek van internationaal type
25 september 2023	

Naam en adres van de instantie	De bevoegde ambtenaar
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	**Campbell, Paul**

Formulier PCT/ISA/201 (tweede blad) (Januari 2004)

ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Informatie over leden van dezelfde octrooifamilie

Nummer van het verzoek om een onderzoek naar de stand van de techniek

NL 2034462

In het rapport genoemd octrooigeschrift	Datum van publicatie	Overeenkomend(e) geschrift(en)	Datum van publicatie
JP 2010027512 A	04-02-2010	GEEN	
US 2005200040 A1	15-09-2005	US 2005200040 A1	15-09-2005
		WO 2005086914 A2	22-09-2005

WRITTEN OPINION

File No.	Filing date *(day/month/year)*	Priority date *(day/month/year)*	Application No.
SN84107	29.03.2023		NL2034462

International Patent Classification (IPC)
INV. B01J37/02 B01J21/18 B01J23/40 B01J35/00 H01M4/86 H01M4/92

Applicant
Sotoodeh Beheer B.V.

This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the application
- ☐ Box No. VIII Certain observations on the application

	Examiner
	Campbell, Paul

Application number

WRITTEN OPINION

NL2034462

Box No. I Basis of this opinion

1. This opinion has been established on the basis of the latest set of claims filed before the start of the search.

2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the application, this opinion has been established on the basis of a sequence listing:

   a. ☐ forming part of the application as filed.

   b. ☐ furnished subsequent to the filing date for the purposes of search,

      ☐ accompanied by a statement to the effect that the sequence listing does not go beyond the disclosure in the application as filed.

3. ☐ With regard to any nucleotide and/or amino acid sequence disclosed in the application, this opinion has been established to the extent that a meaningful opinion could be formed without a WIPO Standard ST.26 compliant sequence listing.

4. Additional comments:

Box No. V Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty	Yes:	Claims	1-10, 16, 17
	No:	Claims	11-15, 18-23
Inventive step	Yes:	Claims	1-10
	No:	Claims	11-23
Industrial applicability	Yes:	Claims	1-23
	No:	Claims	

2. Citations and explanations

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1 JP 2010 027512 A (TOYOTA MOTOR CORP) 4 februari 2010 (2010-02-04)

D2 US 2005/200040 A1 (HARA HIROAKI S [US] ET AL) 15 september 2005 (2005-09-15)

1 In view of the presently available prior art documents, the subject-matter of claims 1-10 is considered novel and involving an inventive step.

1.1 Document D1 is the closest prior art with respect to the subject-matter of claim 1 and discloses in [0020]-[0031]:

A method of producing conductive catalytic particles for heterogeneous catalysis, the method comprises a provision step of providing, in a vessel, porous particles comprising a porous support material carrying a catalyst material (carbon particles including catalyst such as platinum, palladium, ruthenium, iridium or rhodium [0020]); and a step of exposing, in the vessel, the porous particles to supercritical carbon dioxide, thereby disaggregating the catalytic particles [0030]; and a third step of impregnating the particles with electrolyte resin by hot pressing [0031].

1.2 The method of claim 1 differs from that of the prior art in that the impregnation step an comprises exposing, in the vessel, the porous particles to an impregnation solution comprising a conductive polymer in carbon dioxide, thereby impregnating the porous particles with the conductive polymer to obtain the conductive catalytic particles.

1.3 The subject-matter of claim 1 is therefore novel.

1.4 The technical effect of this difference is unknown. The problem to be solved may therefore be considered provision of an alternative method for producing conductive catalytic particles.

1.5 None of the available prior art documents disclose or hint to using a solution solution comprising a conductive polymer in carbon dioxide in order to impregnate the particles with conductive polymer. The solution proposed in claim 1 is therefore not obvious and thus considered to involve an inventive step.

1.6 Claims 2-10 depend on claim 1. The subject-matter of these claims is therefore also considered novel and inventive.

2 The present application does not meet the criteria of patentability, because the subject-matter of claims 11-15 and 18-23 is not new.

2.1 It must first be noted that claims 11-23 are product-by-process claims, specifying a conductive catalytic particle produced by the process according to claim 1 (and various further products including said particle). It is not clear that this specific process leads to distinguishable functional features in the resulting product when compared to similar products of the prior art.

2.2 For instance, the process of D1 described above (§1.1) also leads to conductive catalytic particles consisting of a porous (carbon) support, containing a catalyst material (e.g. Pt), impregnated with a conductive polymer. Furthermore, the particles of D1 are deposited on a membrane for use in a fuel-cell [0031]. The product of D1 therefore takes away the novelty of the product of claims 11-15 and 18-23.

2.3 Furthermore, document D2 also describes in Fig. 2, a porous aerogel support particle (24) including catalytic metal particles (e.g. Pt) (12), whereby a conductive polymer electrolyte (18) is impregnated, having penetrated the pores. Furthermore, the particles of D2 are deposited on a membrane for use in a fuel-cell [0031]. The product of D2 therefore takes away the novelty of the product of claims 11-15 and 18-23.

3 The present application does not meet the criteria of patentability, because the subject-matter of claim 16 and 17 does not involve an inventive step.

3.1 The additional features of claims 16 and 17 describe parameters not associated with any unexpected technical advantage and considered to result from optimisations that the skilled person would carry out without requiring inventive skill.