



AU9519020

(12) PATENT ABRIDGMENT **(11) Document No. AU-B-19020/95**
(19) AUSTRALIAN PATENT OFFICE **(10) Acceptance No. 685247**

- (54) Title
POROUS METAL COMPOSITE BODY
- International Patent Classification(s)
(51)⁶ **B01J 031/06** **B01J 037/18** **C23C 014/18**
- (21) Application No. : **19020/95** (22) Application Date : **21.03.95**
- (87) PCT Publication Number : **WO95/25588**
- (30) Priority Data
- (31) Number (32) Date (33) Country
9405518 **21.03.94** **GB UNITED KINGDOM**
- (43) Publication Date : **09.10.95**
- (44) Publication Date of Accepted Application : **15.01.98**
- (71) Applicant(s)
BRITISH TECHNOLOGY GROUP LIMITED
- (72) Inventor(s)
THOMAS RONALD THOMAS; JAS PAL SINGH BADYAL
- (74) Attorney or Agent
DAVIES COLLISON CAVE , 1 Little Collins Street, MELBOURNE VIC 3000
- (56) Prior Art Documents
DE 3522287
- (57) Claim

1. A method of making a porous Gp VIII metal composite body, comprising metallising a porous substrate, oxidising the metallisation and reducing the metallisation, wherein the oxidation is performed in the gas phase by oxidative plasma and the reduction is performed in the gas phase by reducing plasma.

OPI DATE 09/10/95 APPLN. ID 19020/95
AOJP DATE 23/11/95 PCT NUMBER PCT/GB95/00620



AU9519020

CT)

(51) International Patent Classification ⁶ :
B01J 31/06, 37/18, C23C 14/18

A1

(11) International Publication Number: WO 95/25588

(43) International Publication Date: 28 September 1995 (28.09.95)

(21) International Application Number: PCT/GB95/00620

(22) International Filing Date: 21 March 1995 (21.03.95)

(30) Priority Data:
9405518.3 21 March 1994 (21.03.94) GB

(71) Applicant (for all designated States except US): BRITISH TECHNOLOGY GROUP LIMITED [GB/GB]; 101 Newington Causeway, London SE1 6BU (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): THOMAS, Thomas, Ronald [GB/GB]; Rowan House, Culbo Road, Culbokie, Dingwall, Ross-Shire IV7 8JU (GB). BADIYAL, Jas, Pal, Singh [GB/GB]; 7 Langton Lea, High Shincliffe, Durham DH1 2QF (GB).

(74) Agent: NEVILLE, Peter, Warwick; British Technology Group Limited, Patents Dept., 101 Newington Causeway, London SE1 6BU (GB).

(81) Designated States: AU, CA, FI, JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

685248

(54) Title: POROUS METAL COMPOSITE BODY

(57) Abstract

Microporous polytetrafluoroethylene is metallised with 1 micron platinum, which is plasma-oxygenated then plasma-hydrogenated, whereby to increase the surface area of the platinum. The resulting composite body has applications as a catalyst or electrode.

POROUS METAL COMPOSITE BODY

This invention relates to the production of a composite body comprising porous metal attached to a substrate.

There are applications for such composite bodies in the electrochemical field such as for gas sensors and fuel cells, as well as in the general field of catalysis of chemical reactions and catalytically acting surfaces generally, where high surface areas are required. The substrate is therefore preferably of high surface area, for example it is porous (preferably microporous), and is advantageously of an inert material such as a polymeric material such as a fluoropolymer. Microporous fluoropolymers are well known as chemically, thermally and biologically stable materials used in various phase separation situations, and are advantageously made, for the purposes of the invention, of microporous PTFE (polytetrafluoroethylene) membrane products as disclosed in European Patent 247771, which are useful in a range of applications, including metallised examples produced by for example sputter coating, electrolysis or spin coating. (In spin coating, typically, colloidal catalyst particles are impacted upon a PTFE membrane substrate by the hydrodynamic/centrifugal action of a spinning rotor immersed in the colloid.)

Although many porous Gp VIII metal composite bodies are possible according to the invention, certain materials are of especial interest to workers in the fuel cell, gas sensor and air battery fields, for example the platinum group metals including platinum, palladium and nickel.

In the electrochemical field, it is known that interlocking structures of catalyst and PTFE can be made by simple admixture of dispersions of the materials (e.g. GB Patent 1556452), but the proportion of expensive catalyst to lower-cost PTFE is very high, e.g. 10:3 by mass.

This invention seeks to increase the metal surface area of a given composite body, for example to improve the catalytic activity per unit volume of the composite body or per unit mass of catalyst metal.

US Patent 3715238 teaches the depolarisation of a fuel cell catalyst (e.g. Ru + Pt + some PTFE) by voltage-sweep-treating it in a selected electrolyte at 1 cycle per $\frac{1}{2}$ -20 minutes, whereby, gradually, catalytic metal is deposited at new surfaces so the catalytic metal surface area is gradually increasing. This is too slow as a production method, not to mention the need to rinse and dry or otherwise remove all traces of electrolyte, for some catalytic purposes. Again, the proportion of expensive metal to lower-cost PTFE is very high, nearly $10^4:1$.

US Patent 4540476 teaches the production of a nickel electrode from a porous nickel plaque by applying an alternating potential, such that the nickel dissolves on the oxidising part of the cycle and, on the reducing part of the cycle, oxidised nickel is precipitated as hydroxide. This is performed on nickel sintered on a wire mesh support, thus foregoing the economy, porosity and high surface area per unit volume which binding as a composite with PTFE would have allowed, and also suffers from the above-noted disadvantages of a wet electrolytic process.

According to the present invention, therefore, a porous Gp VIII metal composite body is made by metallising a porous (e.g. ceramic or polymeric) substrate, preferably in the gas phase, (the ratio metal:substrate being preferably less than 1:1, preferably less than 100:1, optionally $<10^4:1$), oxidising the metallisation and optionally or partly or wholly reducing the metallisation, characterised in that the oxidation is performed in the gas phase by oxidative plasma and the reduction is performed in the gas phase by reducing (e.g. ammonia, hydrazine or hydrogen) plasma. The oxidative plasma may be oxygen or other anion (uni- or multi-atomic e.g. bromine) which forms a volatile product with hydrogen. In either case, the gas in question may be present at a pressure of from 0.05 to 1 Torr. Plasma treatment may be performed at a power of from 1 to 30 (preferably 2 to 5) Watts/dm² of substrate, and may continue for from 1 to 20 e.g. 3 to 10 minutes.

The substrate is therefore preferably of an inert material such as a ceramic or polymeric material such as a fluoropolymer such as PTFE or other material at least as stable towards plasma exposure, and may be microporous, with pore sizes of for example up to about 10 microns.

The Gp VIII metal (by which we include alloys) may be a platinum group metal, e.g. platinum, palladium or nickel, or may for example be ruthenium or rhodium or silver.

The invention extends to the composite body so made and to its use as a catalyst, for example in a gas sensor, fuel cell, or electrode. The invention allows the manufacture
5 of a (hitherto unknown) porous metal composite body comprising a porous substrate bearing less than 1% by weight metal, the metal having a surface area at least ten times that of the substrate. The metal may be under 1 micron thick, e.g. 0.05 to 0.1 microns or less, giving maximum catalytic activity at minimum materials cost.

The elements of inconvenience and lack of reproducibility of 'wet' methods such as
10 electrolysis described earlier can be avoided by carrying out the metallisation, the oxidation and the reduction in the gas phase. Gas phase techniques are generally cleaner and quicker and allow greater control over product parameters.

Gas-phase metallisation may be carried out the same way as in the preparation of samples for electron microscopy where the metallic layer conducts away impinging
15 electrons during analysis thus prolonging the life of non-conducting specimens. Additionally the technique allows the production of certain decorative and protective coatings particularly of expensive materials in a cost-effective way.

Good control can be exercised over metal purity and thickness (a major consideration in terms of cost) and hence over the metal loading of the resulting product,
20 e.g. electrode.

Preferably, the next stage of the process of making a composite body according to the invention utilises a cold plasma - so called because the process temperature at the substrate is about 300K, and can be kept below 325K. The composite, let us suppose platinum on microporous PTFE, may be placed in an evacuated chamber and subjected to
25 an oxygen plasma. A controlled amount of the platinum may be oxidised depending upon the ultimate electrical conductance required of the composite. At an appropriate stage the oxidation may be stopped and the oxidised composite subjected to a hydrogen plasma. Under these reducing conditions the oxide reverts to the metal and porosity is induced in

the metallisation layer as interstices are created at points previously occupied by oxide oxygen, the latter being removed by evacuation as water molecules.

This process could clearly be applied to other geometries as well as other metals and substrates. In general the most efficient use of the catalytic entity both in terms of cost and energetics can be made when the surface area is maximised. The disposition and amount of catalyst can be very closely controlled according to ultimate process requirements, for example electrodes for gas sensors, chromatographic separations on treated granules or planar separations with films or tubes.

Preferred embodiments of the
invention will now be described by way of example.

10 EXAMPLE 1: A cylindrical glass glow discharge reactor, 4.5 cm diameter and ½ litre capacity, enclosed in a Faraday cage, is fitted with a gas inlet, a Pirani pressure gauge and a rotary pump attached to a liquid nitrogen cold trap. The reactor is cleaned with detergent, rinsed with isopropyl alcohol and oven dried, followed by a high power (50W) air plasma treatment for 30-40 minutes. A matching network is used to inductively couple
15 a copper coil (4 mm diameter, 9 turns spanning 8 to 15 cm from the gas inlet) wound externally around the reactor to a 13.56 MHz radio frequency source, to generate this plasma. A sample of microporous PTFE is loaded into the reactor, within the region inside the coil. This sample is a sheet of size 100 mm x 150 mm coated by sputtering to a thickness of 1 micron with high purity platinum. The reactor is evacuated to a low
20 pressure, typically 5×10^{-3} Torr, and oxygen of 99.9% purity is introduced at a pressure of 0.05 or 0.1 to 1 Torr, typically 0.1, 0.2 or 0.5 Torr, purged for about 5 minutes. The plasma is then ignited at 30 watts for typically 10 minutes. The radio frequency is then switched off, the gas inlet closed and the reactor evacuated back to base pressure for at least 5 minutes. This introduces oxygen atoms into the platinum.

25 The second stage, a reduction step, is carried out similarly by introducing high purity (99.9%) hydrogen at about 0.05 or 0.1 to 1 Torr, e.g. 0.1, 0.2 or 0.5 Torr, purging for a few minutes, and the plasma ignited at 30 watts for typically 10 minutes. This causes hydrogen to react with the oxygen atoms. The radio frequency is then switched off, the gas inlet closed and the reactor evacuated for 5 minutes. This causes the reacted oxygen to
30 evaporate as water vapour, leaving behind a platinum surface "roughened" by physical



removal of the oxygen from sites where it had reacted and had displaced platinum atoms, hence increasing its surface area. The system is then brought back to atmospheric pressure and the specimen is removed for use.

Further examples of the invention were made using the foregoing apparatus but
5 varying the conditions as follows:-

EXAMPLE 2: Platinum was deposited to various thicknesses, namely 5 μm , 1 μm , 0.1 μm , and to lesser thicknesses, to which it is meaningless to ascribe an exact dimension but which were established to lie in the range 0.05-0.1 μm . After oxidation and reduction as above, all yielded successful catalysts.

10 EXAMPLE 2A: Example 2 was repeated but with the samples located not within the region inside the coil but in the "afterglow" region just outside. This removed the samples from the influence of the highest-energy charged particles and hence lessened ablation of deposited metal by over-energetic impacts from those particles. The remaining charged particles were found to be of an energy distribution which was highly apt for
15 oxidation and reduction. The samples made successful catalysts.

EXAMPLE 3: Instead of just platinum, sputtering of a standard 60:40 gold/palladium alloy was carried out. It was deposited on the PTFE, broadly unchanged in composition, to a thickness of 1 μm . After oxidation and reduction as above, all samples yielded successful catalysts. It is believed that under these conditions the palladium in the
20 deposited alloy has had its surface area increased, leaving the gold unchanged and still a good electrical conductor.

EXAMPLE 4: The sputtered substrate of Example 3 was oxidised under 0.2 Torr oxygen and reduced under 0.1 Torr hydrogen. This was exceptionally successful.

EXAMPLE 5: Examples 3 and 4 were successfully repeated using
25 gold-and-palladium, and (separately) using copper.

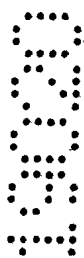
EXAMPLE 6: Examples 3 and 4 were successfully repeated using silver. Oxidation was successful with 0.2 Torr oxygen and only 3 Watts plasma (for 3 minutes).

- 6 -

EXAMPLE 7: Example 2 was repeated with oxidation and reduction both under 0.1 Torr of the respective gas, both under a mild plasma (5 Watts) for 5 minutes. This mild treatment yielded an extremely effective electrochemical material for e.g. amperometric sensor use.

- 5 Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

10



- 7 -

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method of making a porous Gp VIII metal composite body, comprising metallising a porous substrate, oxidising the metallisation and reducing the metallisation, wherein the
5 oxidation is performed in the gas phase by oxidative plasma and the reduction is performed in the gas phase by reducing plasma.
2. A method according to claim 1, wherein the substrate is ceramic or polymeric.
- 10 3. A method according to claim 2, wherein the substrate is a fluoropolymer.
4. A method according to any one of the preceding claims, wherein the body is metallised in the gas phase.
- 15 5. A method according to any one of the preceding claims, wherein the Gp VIII metal is platinum, palladium or nickel.
6. A method according to any one of the preceding claims, wherein the weight ratio metal:substrate is less than 1:1.
20
7. A method according to claim 6, wherein the weight ratio metal:substrate is less than 1:100.
8. A method according to any one of the preceding claims, in which the metallisation is
25 oxidised by oxygen plasma.
9. A method according to any one of the preceding claims, wherein the reduction is performed by hydrogen plasma.



- 8 -

10. A method according to any one of the preceding claims in which the substrate does not exceed 325K during the plasma treatments.

11. A method of making a porous Gp VIII metal composite body substantially as
5 hereinbefore described with reference to the Examples.

12. A porous metal composite body made by a method according to any one of the preceding claims.

10 13. A catalyst comprising a body according to claim 12.

DATED this 2nd day of October 1997

15

British Technology Group Limited

DAVIES COLLISON CAVE

Patent Attorneys for the Applicants



INTERNATIONAL SEARCH REPORT

Intern. Application No.

PCT/GB 95/00620

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B01J31/06 B01J37/18 C23C14/18

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)

IPC 6 B01J C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE-A-35 22 287 (MOC-DANNER GMBH) 2 January 1987 see claims 26,31 ---	1-13
A	PATENT ABSTRACTS OF JAPAN vol. 005 no. 152 (C-073) ,25 September 1981 & JP,A,56 084636 (TANAKA KIKINZOKU KOGYO KK) 10 July 1981, see abstract ---	1-13
A	EP-A-0 306 944 (PHILLIPS PETROLEUM CO) 15 March 1989 see example 4; table 1 ---	1-13
A	US-A-1 865 180 (W.F. FARAGHER) 28 June 1932 see page 2, line 13 - line 21 ---	1-13
-/--		

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in 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 document 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

5 July 1995

Date of mailing of the international search report

14. 07. 95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

Ekhult, H

INTERNATIONAL SEARCH REPORT

Intern. Application No.

PCT/GB 95/00620

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 010 no. 065 (E-388) ,14 March 1986 & JP,A,60 216458 (MATSUSHITA DENKI SANGYO KK) 29 October 1985, see abstract -----	1-13

INTERNATIONAL SEARCH REPORT

information on patent family members

Intern. Appl. No.

PCT/GB 95/00620

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A-3522287	02-01-87	NONE	
EP-A-0306944	15-03-89	US-A- 4818745 JP-A- 1148344	04-04-89 09-06-89
US-A-1865180	28-06-32	NONE	