GOVERNMENT OF INDIA : THE PATENT OFFICE, 214, ACHARYA' JAGADISH BOSE ROAD, CALCUTTA-17. Complete specification AND PROVISIONAL SPECIFICATION No. 143696 dated 9 th April 1976. Application / No. 67/Cal/75 dated 13th January 1975. Acceptance of the complete specification advertised on 14th January 1978.

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"Improvements in or relating to sintered porous metal hydrogen electrodes for use in hydrogen-oxygen fuel cell"

Council of Scientific and Industrial Research, Rafi Marg, New Delhi-1, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860)

The following specification describes the nature of this invention :-

This is an invention by Vanniyur Krishnaswamy Venkatesan, Mandady Venkatakrishna Udupa, Rajam Pattabiraman, Thiruvidiamaruthur Ramanathan Jayaraman and Cherinjethu Puthenveedu Janaki Amma Indira, all of the Central Electro Chemical Research Institute, Karaikudi-3, India, all Indian Citizen.

PRICE: TWO RUPEES

This invention relates to improvements in or relating to the preparation of sintered porous metal hydrogen electrodes for use in low temperature hydrogen-oxygen cell.

Hitherto it has been proposed to fabricate sintered porous metal electrodes of the two layer DSK type with carbonyl nickel as supporting matrix and skeletal Raney nickel as catalyst. The two layers are (1) protective layer either carbonyl nickel or carbonyl nickel and catalyst of suitable particle size and (2) Operating layer-formed with carbonyl nickel and catalyst of

suitable particle size (different from the particle size of those used in the protective layer). A filler such as sodium carbonate or potassium chloride is also included in the operating layer and the filler is removed after the compact is sintered. The electrodes are made by hot pressing at 400-500°C with a pressing pressure of about 1 tonne/cm^2 or by cold pressing, with a pressing pressure of 2 to 5 tonnes/cm^2 and sintering the compact 600-700°C in hydrogen atmosphere.

This is open to the objection that the filler material used for increasing the porosity of the operating layer has to be removed completely by heating in water to about 80°C and after the complete removal of filler material the electrode has to be dried in a vacuum oven. The filler material if not removed completely will affect the electrochemical characteristics of the electrode by slowly reacting with the catalyst.

The object of this invention is to obviate this disadvantage by preparing two layer DSK electrodes with naphthalene as the filler material which can be easily removed while the compact is being sintered at a high temperature.

To these ends the invention broadly consists in the preparation of two layer DSK type electrode with pure nickel as supporting matrix, preserved Raney nickel catalyst containing copper promoter and naphthlene filler by cold pressing and sintering at high temperature in an atmosphere of hydrogen. The protective layer is made with either pure nickel alone or a mixture of pure nickel and preserved Raney nickel catalyst both having a particle size in the range -300 to +400 mesh. The weight ratio of pure nickel to catalyst can be in the range 1:1 to 3:2.

The operating layer is made with a mixture consisting of pure nickel, preserved Raney nickel catalyst and 10% by weight of naphthalene filler. The particle size of the catalyst, pure nickel and filler is in the range -300 to +400 mesh the optimum being -325 +400 mesh. The weight ratio of pure nickel to catalyst is 1:1.

The preserved Raney nickel catalyst is prepared by the method described in literature. The preactivated Raney nickel catalyst is treated with potassium bromate solution for preserving the catalyst. Commercially available nickel-aluminium alloy (50:50) is used for the preparation of the Raney nickel catalyst. The electrodes with the two layers are made by compacting at a pressure of 2 to 5 tonnes/cm^2, the optimum being 2.5 to 3.0 tonnes/cm^2, and sintering the compact at temperature in the range 600° to 800°C, the optimum temperature being 650° - 700°C, in hydrogen atmosphere for 30 mins. The weight ratio of the protective layer to operating layer is in the range 1:1 to 2:3. The sintered electrodes are tested as hydrogen gas diffusion electrode in 6 M KOH at 60°C, the hydrogen gas pressure being 0.8 to 1.2 atm (gauge pressure).

EXAMPLE I:

Preparation of the electrode

Electrode size	: 2.0 cm (dia)
Thickness of the electrode	: 2.5 mm
Protective layer	: pure nickel of particle size -300 +400 mesh
Operating layer	: Pure nickel +preserved Raney nickel of -300 +325 mesh in the weight ratio 1:1
the weight ratio of filler	10% (by weight naphthalene
Weight ratio of protective layer to operating layer	: 1:1 (2g x each)
Pressing Pressure	: 2.54 tonnes/cm^2
Sintering temperature	: 600°C
Catalyst concentration	: 0.3 g/cm^2

Polarisation characteristics:

Electrolyte	: 6 M KOH
Temp.	: 60°C
Hydrogen gas pressure	: 0.9 atm (gauge pressure)
Initial rest potential	: -30 mv (vs hydrogen electrode in the same solution)
Polarisation	: 155 mv at a c.d. of 50ma/cm^2

EXAMPLE - II

Preparation of the electrode

Electrode size	: 4.4. cm dia.
Thickness of the electrode	: 2.5 mm
Protective layer) Operating layer)	: same as in Example I
Filler	: Naphthalene (10%) (by weight)
Weight ratio of protective to operating layer	: 1:1 (8 g. each)
Pressing pressure	: 2.54 tonnes/cm^2
Sintering temperature	: 650^{o}C
Catalyst concentration	: 0.25 g/cm^2

Polarisation characteristics

Electrolyte	: 6 M KOH
Temperature,	: 60^{o}C
Hydrogen gas pressure	: 0.9 atm (gauge pressure)
Initial rest potential	: -40 mv (vs Hydrogen electrode in the same solution)
Polarisation	: 170 mv at a c.d. of 50ma/cm^2

EXAMPLE -III

Electrode preparation:

Electrode size	: 2.0 cm dia.
Thickness of the electrode	: 2.5 mm
Protective layer	: Pure nickel and preserved Raney nickel catalyst in the weight ratio 1:1 Particle size -300 to +400 mesh
Operating layer	: Pure nickel and preserved Raney nickel catalyst in the weight ratio 1:1 Particle size -325 + 400 mesh

Filler	: 10% (by weight) of naphthalene
Weight ratio of operating layer to protective layer	: 1:1 (each 2 g)
Pressing pressure	: 3.048 tonnes/cm^2
Sintering temperature	: 650^{o}C
Catalyst concentration in the operating layer	: 0.3 g/cm^2

Polarisation characteristics

Electrolyte	: 6M KOH
Temp.	: 60^{o}C
Hydrogen gas pressure	: 1.0 atm. (guage pressure)
Initial rest potential	: -40 mv (vs Hydrogen electrode in the same solution)
Polarisation	: 150 mv at a c.d. of 60 ma/cm^2

EXAMPLE IV :

Electrode preparation:

Electrode size	: 2.0 cm dia.
Thickness of the electrode	: 2.5 mm
Protective layer	: Pure nickel of particle size +400 -300 mesh
Operating layer	: Pure nickel + preserved Raney nickel catalyst in the ratio 1:1, and particle size -300 +400 mesh
Filler	: 10% (by weight) potassium chloride
Weight ratio of the protective layer to operating layer	: 1:1 (weight of each layer 2 g)
Pressing pressure	: 3.048 tonnes/cm^2
Sintering temperature	: 650^{o}C
Catalyst concentration	: 0.3 g/cm^2

Polarisation characteristics:

Electrolyte	: 6M KOH
Temp.	: 60^{o}C
Hydrogen gas pressure	: 1.2 atm (gauge pressure)
Initial rest potential	: -10 mv (vs hydrogen electrode in the same solution)
Polarisation	: 150 mv at a c.d. of 30 ma/cm^2

The following are among the main advantages of the invention.

1) The electrode can be prepared by a simple method. The step involving the removal of the filler, if potassium chloride or sodium carbonate is used as filler, is eliminated by the use of naphthalene as a filler.

2) The performance of the electrode prepared with naphthalene as filler is better than that of the electrode made with potassium chloride as filler.

Dated this 6th day of January, 1975.

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([redacted])
ASSTT. PATENTS OFFICER
COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH.

THE PATENT ACT, 1970

COMPLETE SPECIFICATION

SECTION 10

"Improvements in or relating to sintered porous metal hydrogen electrodes for use in hydrogen-oxygen fuel cell".

Council of Scientific and Industrial Research, Rafi Marg, New Delhi-1, India, an Indian registered body incorporated under the Registration of Societies Act (Act XXI of 1860).

The following specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :-

This is an invention by Vanniyar Krishnaswamy Venkatasan, Handady Venkatakrishna Udupa, Thiruvidajmarudhur Ramanathan Jayaraman, Rajam Pattabiraman, Charinjethu Puthenveedu Janaki Amma Indira, all of the Central Electrochemical Research Institute, Karaikudi, 3, Tamil Nadu, India, all Indian citizens.

This invention relates to improvements in or relating to the preparation of sintered porous metal electrodes of the two-layer DSK(Doppel Skeletal Katalysator) type containing Raney nickel catalysts for use as hydrogen electrode in low-temperature Hydrogen-Oxygen Fuel Cell. The low-temperature Hydrogen-Oxygen fuel cells will serve as power source and energy storage device with varied applications.

Our copending Indian Patent application No.32/Cal/75 relates to the preparation of sintered porous metal electrodes of the two-layer DSK type (Doppel skeletal Katalysator) containing silver catalysts to be used as oxygen electrodes in low-temperature Hydrogen Oxygen Fuel Cells.

In comparison our present investigation is for similar electrodes for use as hydrogen electrodes in similar fuel cells, but as distinguished from those of 32/Cal/75 no silver catalysts are used in their preparation. The use of silver catalyst as in the said co-pending application for the preparation of the said electrodes which forms its subject matter is hereby excluded from the scope of the present investigation.

The sintered porous metal electrodes of the two-layer DSK(Doppel skeletal Katalysator) type for use as hydrogen electrode in the low-temperature Hydrogen-Oxygen fuel cell have hitherto been prepared with a protective layer made of either carbonyl nickel(or pure nickel) only or carbonyl nickel (or pure nickel) in combination with Raney nickel catalysts of suitable particle size and an operating layer formed with carbonyl nickel, Raney nickel catalysts and a filler such as sodium carbonate, potassium chloride. The electrodes are made either by hot-pressing at 400-500°C with a pressing pressure of 1 tonne/cm^2 or by cold pressing with a pressing pressure of 2-5 tonnes/cm^2 and sintering the compact at 600-700°C in hydrogen atm.

The drawback of the hitherto known process is that the filler material used for increasing the porosity of the operating layer has to be removed completely by heating in water to about 80°C and after complete removal of the filler, the electrode has to be dried in a vacuum oven.If the filler material is not removed completely, it will affect the electrochemical characteristics of the electrode by slowly reacting with the catalyst.

The main object of this invention is to prepare sintered porous metal electrodes of the two-layer DSK (Doppel skeletal Katalysator) type for use as hydrogen electrode in low-temperature hydrogen-oxygen fuel cell using pure nickel powder to form the protective layer and a mixture of pure nickel, preserved skeletal Raney nickel catalyst with copper promotor and naphthalene as the filler, to form the operating layer, by compacting and sintering at high temperature.

The sintered porous metal electrodes of the two-layer DSK(Doppel skeletal Katalysator) type for use as Hydrogen electrodes are prepared with nickel and with preserved skeletal Raney nickel catalyst containing copper promotor and naphthalene as the filler, in the operating layer and pure nickel alone in the protective layer, by cold pressing at a pressure of 2-5 tonnes/cm^2 and sintering the compact at temperatures in the range 600-800°C.

The electrode so prepared using naphthalene as the filler can be used directly, as the filler naphthalene has been removed during sintering process, thus avoiding one more step involving the removal of filler after sintering and drying in a vacuum oven.

The present invention consists of a process for the preparation of sintered porous metal electrode of the two-layer DSK(Doppel skeletal Katalysator) type for use as hydrogen electrode in low-temperature Hydrogen-

Oxygen fuel cell. The electrode consists of one protective layer containing pure nickel and an operating layer consisting of pure nickel, preserved skeletal Raney nickel catalyst containing copper promotor and naphthalene as filler by cold pressing and sintering at high temperatures in hydrogen atmosphere. The sintered porous metal electrodes of the two layer DSK(Doppel Skeletal Katalysator) type for use as hydrogen electrodes are made by taking suitable amount of the components for the protective layer and operating layer in the weight ratio 1:1 to 2:3, the preferred ratio being 1:1, cold pressing at a pressure of 2 to 5 tonnes/cm^2, the preferred pressing pressure being 2.5 - 3 tonnes/cm^2 and sintering the compact at temperatures in the range 600-800°C, the preferred temperature being 650°-700°C in hydrogen atmosphere for 30 minutes. The operating layer consists of pure nickel, preserved skeletal Raney nickel of particle size in the range 45-53 microns, the preferred size being 45-50 microns and naphthalene as filler, the components well-mixed together, while the protective layer consists of pure-nickel of particle size in the range 37-45 microns. The weight ratio of the pure nickel to the catalyst in the operating layer is 1:1 and the filler concentration is 10% by weight. Commercially available nickel aluminium alloy(50:50 by weight) which consists of Ni_2Al_3 and $NiAl_3$, is used for the preparation of skeletal Raney nickel catalyst with copper as promotor(the concentration being 5 mg of Cu/gm of Raney nickel) by the method available in literature. The preactivated catalyst is preserved by treatment with potassium bromate, as described in literature. The electrodes so prepared were tested as hydrogen gas diffusion electrodes in 6N KOH at 60°C with hydrogen gas pressure of 0.8 - 1.2 atm.(gauge pressure).

Few typical examples are given below:

EXAMPLE I:

Preparation of the electrode

Electrode size	2.0 cm(dia.)
Thickness of the electrode	2.5 mm
Protective layer	Pure nickel of particle size 37-45 microns
Operating layer	Pure nickel + preserved Raney nickel of 45-50 microns in the weight ratio 1:1
The weight ratio of filler	10% (by weight) naphthalene
Weight ratio of protective layer to operating layer	1:1 (2 g each)
Pressing pressure	2.54 tonnes/cm^2
Sintering temperature	600°C
Catalyst concentration	0.3 g/cm^2

Polarisation characteristics:

Electrolyte	6N KOH
Temp.	60°C
Hydrogen gas pressure	0.9 atm(gauge pressure)
Initial rest potential	-30 mv(vs hydrogen electrode in the same solution)
Polarisation	155 mv at a c.d. of 50 ma/cm^2

EXAMPLE-II

Preparation of the electrode

Electrode size	4.4 cm dia.
Thickness of the electrode	2.5 mm
Protective layer Operating layer	Same as in Example I
Filler	Naphthalene(10% by weight)
Weight ratio of protective to operating layer	1:1 (8 g.each)
Pressing pressure	2.54 tonnes/cm^2
Sintering temperature	650°C
Catalyst concentration	0.25 g/cm^2

Polarisation characteristics:	
Electrolyte	6N KOH
Temperature	60°C
Hydrogen gas pressure	0.9 atm(gauge pressure)
Initial rest potential	-40 mV(vs Hydrogen electrode in the same solution)
Polarisation	170 mv at a c.d. of 50 ma/cm^2

EXAMPLE-III

Electrode preparation:	
Electrode size	2.0 cm dia.
Thickness of the electrode	2.5 mm
Protective layer	Pure nickel and preserved Raney nickel catalyst in the weight ratio 1:1
	Particle size 37-45 microns
Operating layer	Pure nickel and preserved Raney nickel catalyst in the weight ratio 1:1
	Particle size 45-50 microns
Filler	10%(by weight) of naphthalene
Weight ratio of operating layer to protective layer	1:1 (each 2 g)
Pressing pressure	3.048 tonnes/cm^2
Sintering temperature	650°C
Catalyst concentration in the operating layer	0.3 g/cm^2
Polarisation characteristics	
Electrolyte	6N KOH
Temp.	60°C
Hydrogen gas pressure	1.0 atm.(gauge pressure)
Initial rest potential	-40 mV(vs Hydrogen electrode in the same solution)
Polarisation	150 mv at a c.d. of 60 ma/cm^2

EXAMPLE IV:

Electrode preparation:

Electrode size	2.0 cm dia.
Thickness of the electrode	2.5 mm
Protective layer	pure nickel of particle size 37-45 microns
Operating layer	Pure nickel + Preserved Raney nickel catalyst in the ratio 1:1 and particle size 45-50 microns
Filler	10%(by weight)potassium chloride
Weight ratio of the protective layer to operating layer	1:1(weight of each layer 2 g)
Pressing pressure	3.048 tonnes/cm^2
Sintering temperature	650°C
Catalyst concentration	0.3 g/cm^2

Polarisation characteristics:

Electrolyte	6N KOH
Temp.	60°C
Hydrogen gas pressure	1.2 atm(gauge pressure)
Initial rest potential	-10mV(vs Hydrogen electrode in the same solution)
Polarisation	150 mv at a c.d.of 30 ma/cm^2

The following are the main advantages of the invention:

The electrode can be prepared by a simple method as the step involving the removal of filler, if potassium chloride or sodium carbonate is used as filler, is eliminated.

The electrodes prepared with naphthalene as filler show a polarisation lower by about 50 mv, than that the electrode prepared with potassium chloride as filler, at the same current density.

WE CLAIM:

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1. An improved process for the preparation of sintered porous metal hydrogen electrodes of the two layer DSK(Doppel skeletal Katalysator) type for use in Low Temperature Hydrogen-Oxygen Fuel cells comprising a protective and an operative layer, characterised in that the protective layer is made of pure nickel of 37/45 micron particle size and the operating layer is made up of pure nickel, preserved skeletal Raney nickel catalyst containing copper as a promotor in particle size of 45/53 microns in 1:1 ratio and 10% by weight of naphthalene as filler by cold pressing and sintering the compact in hydrogen atmosphere.

2. The process as claimed in claim 1 wherein the ratio between the two layers is in the range of 1:1 to 2:3 by weight.

3. The process as claimed in claim 1 and 2 wherein the cold pressing is done at a pressure of 2-5 tonnes/cm^2 and sintering is effected at a temperature of 600-800°C.

4. The process as claimed in claim 3 wherein the cold pressing is done at a pressure of 2.5 - 3 tonnes/cm^2 and sintering is effected at 650°-700°C for a period of 30 minutes in hydrogen atmosphere.

5. The process as claimed in any of the preceding claims wherein the amount of copper used as a promotor is 5 mg of Cu per gram of Raney nickel.

Dated this 7th day of April, 1976.

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