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"Improvements in or relating to sintered porous metal electrodes containing silver catalysts for use as oxygen electrodes in low temperature hydrogen-oxygen fuel cell."

Council of Scientifica and Industrial Research, Rafi Marg, NewDelhi-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, Handady Venkatakrishna Udupa, Kaliappan Shanmugam Arumugasamy Gnanasekharan, Rajam Sastrigal Pattabiraman, Tiruvidaimarudhur Ramanathan Jayaraman, Charinjethuputhenveedu Janaki Amma Indira and Ramaswamy Chandrasekaran, all of the Central Electrochemical Research Institute, Karaikudi-3, Tamil Nadu, India, all Indian citizens.

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Hitherto it has been proposed to use sintered porous metal electrodes of two layer DSK type with Raney silver as catalyst and carbonyl nickel as the supporting matrix. One of the layers of the two layer DSK electrode called the protective layer contains either carbonyl nickel or carbonyl nickel and Raney silver of suitable particle size. The second layer, heretofore called (or known as) operating layer contains Raney silver and carbonyl nickel in the weight ratio, varying from 1:1 to 1:0.40 and potassium chloride as filler material. The two layer DSK

electrodes are made by hot pressing in the temperature range 300-500°C at a pressure of 1.015 tonne/cm^2. After hot pressing the filler material is removed and then the aluminium in the Raney silver alloy is leached out with potassium hydroxide solutions.The polarisation characteristic of two layer DSK type electrode containing about 0.3 - 0.4 g/cm^2 Raney silver catalyst, reported in literature is about 100 mv at a c.d. of 60 ma/cm^2. The polarisation of three layer DSK type oxygen electrode containing about 5% by weight of silver in the operating layer has been reported as 220 mv at a c.d. of 60 ma/cm^2.

This is open to the objection that the preparation of Raney-silver i.e., silver-aluminium alloy in the powder form is quite an involved process and proper quenching of the alloy melt is necessary for the preparation of the alloy in powder form.Further the electrodes cannot be prepared by cold-pressing and sintering at high temperature, i.e., above 600°C along with nickel containing supporting matrix as at these temperatures an alloy of the composition Ni Al will be formed which is not attacked by KOH. Thus the Raney silver suitable for oxygen electrodes is not obtained by this. The electrodes should,therefore, be hot pressed and the aluminium in the silver-aluminium alloy leached out by treatment with KOH. The object of this invention is to obviate these disadvantages by employing the following catalysts, silver formed in situ from silver carbonate(I), silver-cadmium formed on Al_2O_3 carrier(II), acetylene black impregnated with silver(III) in the place of Raney-silver in the two layer DSK electrodes used as oxygen electrode in the hydrogen-oxygen fuel cell.

To these ends the invention broadly consists in making sintered porous metal electrodes of the two layer DSK type, with Pure nickel as the supporting matrix and any one of the following catalyst, silver (formed in situ from silver carbonate) (I), silver-cadmium on Al_2O_3 carrier (II) and acetylene black impregnated with silver(III) in the operating layer. The operating layer contains Pure nickel and the catalyst in

suitable proportions. A filler such as potassium chloride or naphthalene is added to the extent of about 10% by weight, while making the pellet before pressing and sintering. The catalyst, 'Pure' nickel and filler material have a particle size in the range -220 to +400 mesh, the optimum size being -300 +400 mesh The protective layer consists of either pure carbonyl nickel or a mixture of 'Pure' nickel and the catalysts. The electrodes are made by cold pressing with a pressing pressure of 2 to 5 tonne/cm^2 and sintered at a temperature range of 600° to 800°C the optimum temperature being 600° to 650°C. The sintering is carried out in an atmosphere of hydrogen or nitrogen. The operating layer of the electrode containing catalyst (I) is prepared by forming the silver in situ from silver carbonate. The silver carbonate is mixed with 'Pure' nickel, in the ratio ranging from 0.5:1 to 1:0.5 the optimum ratio being 1:1, along with a filler material. The amount of filler used is 10% by weight of the total mix.

The catalyst (II) is prepared by coprecipitating silver oxide, cadmium hydroxide and aluminium hydroxide from a solution containing 170 g/l of silver nitrate, 81 g of $Cd(NO_3)_2$ 4 H_2O and 320 g of aluminium nitrate with 6 normal potassium hydroxide. The precipitate is washed and dried at 110-120°C. The dried mass is then heated at 700°C in nitrogen atmosphere for 2 to 6 hours. The catalyst has been found to contain 40% by weight silver, 14% cadmium and the rest Al_2O_3. The product is then powdered to the desired particle size and mixed with 'Pure' nickel and filler material and the electrodes are prepared as described above. The ratio of catalyst to 'Pure' nickel can be in the range 3:1 to 1:5 the optimum ratio being 1:3 to 1:4.

The catalyst (III) acetylene black impregnated with silver is prepared by the following method. The required quantity of acetylene black is soaked in a silver nitrate solution of concentration 5 to 15% (by weight) containing 0.5% by weight of Triton X-100 as wetting agent, for a period of about 40 to 80 hours. The acetylene black is then filtered, dried and decomposed in hydrogen atmosphere at 450°C for 90 mins. The amount of silver present in

the acetylene (each) varies from 15 to 30%(by weight) depending upon the concentration of silver nitrate solution taken initially. Pure nickel is mixed with catalyst (III), the catalyst concentration being in the range 1-3% (by weight), along with filler material. The sintered electrode is prepared as given above. The optimum catalyst concentration is 2% by weight.

The two layer DSK electrodes after removal of the filler material, if potassium chloride has been used as the filler, is used as oxygen electrode at a gas pressure of 1 to 1.5 atm (gauge pressure) and the polarisation characteristics of the electrode compared with the reported values of an electrode containing Raney-silver catalyst.

EXAMPLE I:

Preparation of two layer DSK type electrode containing Catalyst(I)

Electrode size	: 2.2 cm dia.
Weight of the operating layer including the filler material	: 2 g
Weight of the protective layer consisting of Pure nickel of -325 to +400 particles	: 2 g
Ratio of Pure nickel to silver carbonate both having a particle size of -300 to +325	: 1:1
Amount of potassium chloride filler used	: 10% by weight
Pressing pressure	: 3.048 tonne/cm^2
Sintered at 600°C in nitrogen atmosphere for 1 hour	
Amount of silver catalyst	: 0.17 g/cm^2

Polarisation characteristics:

Electrolyte	: 6 M KOH
Temperature	: 60°C
Oxygen gas pressure	: 1.1 - 1.2 atm (gauge pressure)
Initial rest potential	: +1030 mv (vs hydrogen electrode in the same solution)
Polarisation	: 240 mv at a c.d. of 60 ma/cm^2

EXAMPLE-II

Preparation of two layer DSE electrode containing catalyst (II)

Electrode size	: 2.2 cm.(dia.)
Weight of the operating layer (including filler)	: 2 g
Weight of the protective layer consisting of Pure nickel of particle size -325 to +400	: 2 g
Ratio of catalyst Ag. Ca(Al_2O_3) to nickel	: 1:4
to nickel particle size of the catalyst and Pure nickel powders	: -300 to +325
Amount of potassium chloride filler	: 10% by weight
Pressing pressure	: 2.54 tonne/cm^2
Sintering temperature	: 600°C in Nitrogen atmosphere
Amount of silver catalyst	: 0.045 g/cm^2

Polarisation characteristics:

Electrolyte	: 6 M KOH
Temp.	: 60°C
Oxygen gas pressure	: 0.9 atm(gauge pressure)
Initial rest potential	: +920 mv (vs Hydrogen electrode in the same solution)
Polarisation	: 240 mv at a c.d. of 60 ma/cm^2

EXAMPLE-III

Preparation of two layer DSK type electrode containing catalyst (III). The preparation conditions are the same as in example II except for the filler. Potassium thloride is used instead of naphthalene.(10% by weight).

Polarisation characteristics:

Electrolyte	: 6 M KOH
Temperature	: 60°C
Oxygen gas pressure	: 1.4 atm.
Initial rest potential	: +940 mv (vs Hydrogen electrode in the same solution)

EXAMPLE IV:

Preparation of Two layer DSK type electrode using catalyst (III)

Electrode size	: 2.2 cm dia.
Weight of catalyst, Pure nickel and filler used for the operating layer	: 2 g
Catalyst concentration	: 0.04 g
Particle size	: -300 to +325
Filler	: Potassium chloride (10% by weight)

Protective layer:

Weight of Pure nickel	: 1.96 g
Weight of catalyst	: 0.04 g
Pressing pressure	: 3.048 tonne/cm^2
Sintering temperature	: 650°C in hydrogen atmosphere
Amount of silver present in the electrode	: 0.003 g/cm^2

Polarisation characteristics:

Electrolyte	: 6 N KOH
Temperature	: 60°C
Oxygen gas pressure	: 1.5 atm.(gauge pressure)
Initial rest potential	: +980 mv (vs Hydrogen electro in the same solution)
Polarisation	: 185 mv at 60 ma/cm^2

The following are among the main advantages of the invention

1)The method of preparation of catalysts is simple and does not involve any critical conditions.

2)The step involving leaching of aluminium from the sintered electrode is eliminated.

3)When naphthalene is used as a filler, the electrode can be used immediately after sintering.

4)The amount of silver catalyst used is considerably less than those reported in literature.

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THE PATENTS ACT, 1970

COMPLETE SPECIFICATION

SECTION 10

" Improvements in or relating to sintered porouds metal electrodes containing silver catalysts for use as oxygen electrodes in low temperature 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 of1860)

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

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This invention relates to improvements in or relating to the preparation of sintered porous metal electrodes of the two-layer DSK type containing silver catalysts to be used as oxygen electrode in low-temperature H_2-O_2 Fuel cells. The Fuel cells will serve as a power source and an energy storage device with varied applications.

The sintered porous metal electrodes of the two-layer DSK type for use as oxygen 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 of suitable particle size and an operating layer made of carbonyl nickel or pure nickel in combination with Raney silver (silver-aluminium alloy) and potassium chloride as filler. The weight ratio of carbonyl nickel (or pure nickel) to Raney silver in the operating layer is in the range 1:1 to 1:0.4. The electrodes are made by hot pressing at a temperature in the range 300°-500°C and at a pressing pressure of 1.016 tonnes/ cm^2. After the electrode is made by hot pressing the filler is removed by treatment with hot water and the aluminium in the Raney silver is removed by leaching with potassium hydroxide.

The following are the drawbacks of the hitherto known process:

i)The preparation of Raney silver in powder form is quite an involved process and proper quenching of the alloy melt is necessary for the preparation of the alloy in powder form.

ii)The electrodes have to be hot-pressed and cannot be prepared by cold-pressing and sintering at high temperature, i.e., above 600°C.

The main object of the invention is to prepare sintered porous metal electrodes of the two-layer DSK type with silver catalysts other than Raney silver catalyst.

According to the present invention, there is provided a process for the preparation of sintered porous metal electrodes of the two-layer DSK (Doppel-skeletal-Katalysator) type for use as oxygen electrode in low temperature hydrogen-oxygen fuel cell by mixing carbonyl nickel or pure nickel with a silver catalyst characterised in that the silver catalyst is prepared directly in powder form by (i) forming silver in situ from silver carbonate, (ii) forming silver cadmium on alumina carrier, or (iii) impregnating acetelene black with silver, further characterised in that pure nickel or carbonyl nickel is mixed with any of the silver catalysts thus obtained using naphthalene as filler to form an operating layer, compacting by cold pressing the operating layer, with pure or carbonyl nickel as a protective layer and sintering the compact in the range of 600°C to 800°C in hydrogen or inert atmosphere.

The protective and operating layer are compacted by cold pressing at a pressing pressure of 2 to 5 tonnes cm^2 and sintering the compact in the range of temperatures from 600-800°C in hydrogen or inert atmosphere.

Any of the silver catalysts may be mixed with pure nickel or carbonyl nickel in the weight ratio 1:1 to 1:0.025, the particle size of both being in the range 45-53 microns and naphthalene as filler 10% by weight.

Pure or carbonyl nickel of particle size 10 to 30 microns is used as the protective layer.

The relative amounts of the protective and operating layers may vary between 1:1 to 2:3, at a pressing pressure of 2 to 5 tonnes/cm^2 by cold pressing.

The concentration of silver in the electrode is in the range 3-200 mg/cm^2.

Silver cadmium may be formed on alumina using silver and cadmium in the range at 32 to 41% and 5 to 14% by weight respectively.

Acetylene black may be impregnated with silver of concentration in the range 15 to 30% by weight.

The three silver catalysts were prepared as follows:

i)The required amount of silver carbonate is mixed with pure nickel in the ratio ranging from 1:2 to 2:1 along with the required quantity of the filler to form the operating layer of the two-layer DSK electrode which on sintering after compaction gives silver dispersed in the operating layer.

ii)Silver oxide, cadmium hydroxide and aluminium hydroxide are co-precipitated from a solution containing silver nitrate of concentration in the range 203 g/l to 159 g/l, cadmium nitrate (hydrated) of concentration in the range 38 g/l to 94 g/l and aluminium nitrate(hydrated) of concentration 320 g/l, with 6N potassium hydroxide. The precipitate is washed and dried and the dried mass is heated at 400°C in nitrogen atmosphere for 2-6 hours to get a catalyst containing silver in the range 41 to 32% by weight,

cadmium 5 to 14% by weight and the rest being Al_2O_3 depending upon the initial concentrations of the constituents in solution.

iii)The catalyst, acetylene black impregnated with silver is prepared by soaking required quantity of acetylene black in a silver nitrate solution of concentration 5-15% by wt. and containing 0.5% by wt. of Triton X-100 as wetting agent for a period of 40-80 hours. The acetylene black is then filtered, dried and decomposed in hydrogen atm. at 450°C for 90 minutes. The amount of silver present in the acetylene black was found to vary from 15-30% by wt.depending upon the initial concentration of silver nitrate taken.

The method of preparation of these three catalysts are very simple and does not involve any critical condition and can be obtained in powder form. The concentration of silver catalysts is relatively small when incorporated in the operating layer of the two-layer DSK type electrode.

It has been found that naphthalene can be used as a filler instead of potassium chloride which avoids the additional step of removing the filler after sintering.

The electrode thus consists of one protective layer made of pure nickel of suitable particle size and an operating layer containing pure nickel, one of the three silver catalysts and naphthalene as filler. The required quantity of the components of the two layers are taken, compacted by cold pressing and sintered at high temperature in hydrogen or nitrogen. The filler, naphthalene, is removed during sintering process.

The sintered porous metal electrodes are made by taking suitable amounts of the components for the protective layer and operating layer in the weight ratio 1:1 to 2:3, cold pressing at a pressure of 2-5 tonnes/cm^2, the preferred pressure being 2.5 to 3.0 tonnes/cm^2 and sintering the compact at temperatures in the range 600-800°C, the preferred temperature being 650°C - 700°C in hydrogen or nitrogen atm. for 30 minutes. The particle size of the pure nickel in the protective layer is in the range of 37-45 microns while the particle size of pure nickel, silver catalysts and the filler in the operating layer is in the range 45-53 microns, the preferred range being 45-50 microns. The weight ratio of pure nickel to catalysts in the operating layer can be in the range 1:1, 1:4 and 1:0.2 for the three silver catalysts respectively. The silver catalysts are prepared by the procedures already described above. The electrodes so prepared were tested as oxygen electrode at an oxygen gas pressure of 1-1.5 atm. (gauge pressure) and the polarisation characteristics of the electrodes were found comparable with the reported values of an electrode containing Raney silver as catalysts.

Few typical examples are given below:

EXAMPLE I:

Preparation of two layer DSK type electrode containing Catalyst(I)

Electrode size	: 2.2 cm. dia.
Weight of the operating layer including the filler material	: 2 g
Weight of the protective layer consisting of pure nickel of 37 to 45μ	: 2 g

Ratio of pure nickel to silver carbonate both having a particle size of 45 μ to 50 μ	: 1:1
Amount of potassium chloride filler used	: 10% by weight
Pressing pressure	: 3.048 tonnes/cm^2

Sintered at 600°C in nitrogen atm.for 1 hr.

Amount of silver catalyst	: 0.17 g/cm^2

Polarisation characteristics:

Electrolyte	: 6N KOH
Temperature	: 60°C
Oxygen gas pressure	: 1.1 - 1.2 atm(gauge pressure)
Initial rest potential	: +1030 mV(vs hydrogen electrode in the same solution)
Polarisation	: 240 mV at a c.d. of 60ma/cm^2

EXAMPLE-II

Preparation of two-layer DSK electrode containing catalyst(II)

Catalyst contains 34% by wt. of silver, 12% by wt.of cadmium and the rest Al_2O_3

Electrode size	: 2.2 cm (dia.)
Wt.of the operating layer (including filler)	: 2 g
Wt.of the protective layer consisting of pure nickel of particle size 37 μ to 45 μ	: 2 g
Ratio of catalyst Ag.Cd(on Al_2O_3) to pure nickel	: 1:4
Particle size of the catalyst and pure nickel powders	: 45 μ to 50 μ
Amount of naphthalene filler used	: 10% by wt.
Pressing temperature	: 2.54 tonnes/cm^2
Sintering temperature	: 600°C in Nitrogen atmosphere
Amount of silver catalyst	: 0.045 g/cm^2

Polarisation characteristics:

Electrolyte	: 6 N KOH
Temp.	: 60°C
Oxygen gas pressure	: 0.9 atm(gauge pressure)
Initial rest potential	: +920 mV(vs Hydrogen electrode in the same solution)
Polarisation	: 240 mV at a c.d. of 60ma/cm

EXAMPLE-III

The preparation conditions are the same as in Example II except for the filler. Potassium chloride is used instead of naphthalene as filler.

Polarisation characteristics:

Electrolyte	: 6N KOH
Temperature	: 60°C
Oxygen gas pressure	: 1.4 atm. (gauge pressure)
Initial rest potential	: +940 mV(vs Hydrogen electrode in the same solution)
Polarisation	: 240 mV at a c.d. of 40 ma/cm^2

EXAMPLE IV:

Preparation of catalyst(III):

Amount of acetylene black taken	: 10 g
Total volume of silver nitrate solution taken	:200 ml
Amount of silver nitrate in the solution	: 20 g
Wetting agent(Triton X 100) concentration	: 0.5%
Soaking time	: 72 hours

The soaked acetylene black was filtered, dried and heated in a hydrogen atmosphere at 450°C for 90 mins. The amount of silver present in the acetylene black has been found as 24%(by weight).

Preparation of two-layer DSK type electrode containing catalyst III:

Electrode size	: 2.2 cm. dia.
Weight of catalyst, pure nickel and filler used for the operating layer	: 2 g
Catalyst concentration	: 0.04 g
Particle size	: 45 to 50 μ
Filler	: Potassium chloride(10% by wt.)

Protective layer:

Weight of pure nickel	: 1.96 g
Weight of catalyst	: 0.04 g
Pressing pressure	: 3.048 tonnes/cm^2
Sintering temperature	: 650°C in hydrogen atmosphere
Amount of silver present in the electrode	: 0.003 g/cm^2

Polarisation characteristics:

Electrolyte	: 6N KOH
Temperature	: 60°C
Oxygen gas pressure	: 1.5 atm.(gauge pressure)
Initial rest potential	: +980 mV(vs Hydrogen electrode in the same solution)
Polarisation	: 250 mV at 21 ma/cm^2

EXAMPLE V:

The preparation conditions are the same as in Example IV except for the filler. Naphthalene (10% by wt.) is used instead of potassium chloride as filler.

Polarisation characteristics:

Electrolyte	: 6N KOH
Temperature	: 60°C
Oxygen gas pressure	: 1.3 atm(gauge pressure)
Initial rest potential polarisation	:190 mV at a c.d. of 40 ma/cm^2

The polarisation characteristics of two layer DSK type electrode containing about 0.3 - 0.4 g/cm^2 Raney silver catalyst, reported in literature is about 100 mV at a c.d. of 60 ma/cm^2. The polarisation of three layer DSK type oxygen electrode containing about 5% by weight of silver in the operating layer has been reported as 220 mV at a c.d. of 60 ma/cm^2.

The following are among the main advantages of the invention:

i)The method of preparation of catalysts is simple and does not involve any critical conditions;

ii)The step involving leaching of aluminium from the sintered electrode is eliminated;

iii)When naphthalene is used as the filler, the electrode can be used immediately after sintering;

iv)The amount of silver catalyst used is considerably less than those reported in literature.

WE CLAIM:

1. A process for the preparation of sintered porous metal electrodes of the two-layer DSK (Doppel-skeletal-Katalysator) type for use as oxygen electrode in low temperature hydrogen-oxygen fuel cell by mixing carbonyl nickel or pure nickel with a silver catalyst characterised in that the silver catalyst is prepared directly in powder form by (i) forming silver <u>in situ</u> from silver carbonate, (ii) forming silver cadmium on alumina carrier, or (iii) impregnating acetylene black with silver further characterised in that pure nickel or carbonyl nickel is mixed with any of the silver catalysts thus obtained using naphthalene as filler to form an operating layer, compacting by cold pressing the operating layer, with pure or carbonyl nickel as a protective layer and sintering the compact in the range of 600°C to 800°C in hydrogen or inert atmosphere.

2. A process as claimed in claim 1 wherein the protective and operating layer are compacted by cold pressing at a pressing pressure of 2 to 5 tonnes cm^2 and sintering the compact in the

range of temperatures from 600-800°C in hydrogen or inert atmosphere.

3. A process as claimed in claim 1 or 2 wherein any of the silver catalysts are mixed with pure nickel or carbonyl nickel in the weight ratio 1:1 to 1:0.025, the particle size of both being in the range 45-53 microns and naphthalene as filler 10% by weight.

4. A process as claimed in any of the preceding claims wherein pure or carbonyl nickel of particle size 10 to 30 microns is used as the protective layer.

5. A process as claimed in any of the preceding claims wherein the relative amounts of the protective and operating layers vary between 1:1 to 2:3, at a pressing pressure of 2 to 5 tonnes/cm^2 by cold pressing.

6. A process as claimed in any of the preceding claims wherein the concentration of silver in the electrode is in the range 3-200 mg/cm^2.

7. A process as claimed in any of the preceding claims wherein silver cadmium is formed on alumina, using silver and cadmium in the range at 32 to 41% and 5 to 14% by weight respectively.

8. A process as claimed in any of the preceding claims wherein acetylene black is impregnated with silver of concentration in the range 15 to 30% by weight.

9. A process as claimed in any of the preceding claims wherein a process for the preparation of sintered porous metal electrodes of the two-layer DSK (Doppel-skeletal-Katalysator) type

for use as oxygen electrode in low temperature hydrogen-oxygen fuel cell substantially as herein before described.

Dated this 3rd day of April, 1976.

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