

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
29 June 2006 (29.06.2006)

PCT

(10) International Publication Number
WO 2006/066973 A2

(51) International Patent Classification: Not classified

(21) International Application Number:
PCT/EP2005/014180

(22) International Filing Date:
23 December 2005 (23.12.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
MI2004A002468
23 December 2004 (23.12.2004) IT

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(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV,
LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI,
NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG,
SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US,
UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT,
RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished
upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: METHOD FOR THE PREPARATION OF A NICHEL CERMET FOR SOLID OXIDE FUEL CELLS

(57) Abstract: A method for the preparation of a ceramic-metallic composition (cermet) consisting of at least 70% by weight of a solid material comprising from 35 to 70% by weight of a metallic nickel phase and from 65 to 30% by weight of at least one oxide selected from oxides of transition metals and lanthanides, comprising the following steps in succession: i) preparing a mixture of powders comprising metallic nickel and at least one oxide different from nickel oxide, selected from oxides of transition metals and lanthanides; ii) laying said mixture of powders on a suitable surface, in the form of a layer having a thickness ranging from 2 to 1500 µm; iii) heating said layer under oxidative conditions until obtaining the desired sintering degree; and, optionally, iv) reducing the nickel oxide in the sintered product to metallic Ni.



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5 METHOD FOR THE PREPARATION OF A NICKEL CERMET FOR SOLID OX-
IDE FUEL CELLS

The present invention relates to a method for the preparation of a nickel cermet which can be used in the manufacturing of solid oxide fuel cells (SOFC).

10 More specifically, the present invention relates to a method for the preparation of a sinterable composition comprising metallic nickel in close contact with certain ceramic materials, capable of promoting anodic reactions in a fuel cell.

15 Solid oxide fuel cells (SOFC) comprising a solid electrolyte consisting of a mixture of yttrium oxide (yttria) (Y_2O_3) and zirconium oxide (zirconia) (ZrO_2), an anode made up of a nickel/zirconium oxide cermet and a cathode of lanthanum manganite (LaMnO_3), are known in the art. This sub-
20 ject is generally dealt with, for example, in the publication "Ullmann's Encyclopedia of Industrial Chemistry, Vol. A 12, Ed.1989, pages 80-82", whereas many other publications on various aspects of the fuel cell and particularly SOFC technology are available to experts in the field in
25 specialized literature.

The nickel/zirconium oxide cermet used as anodic material normally consists of a dispersion of metallic nickel in zirconium oxide stabilized in cubic crystalline form with from 5 to 20% by weight of yttrium oxide.

5 The processes for the preparation of said cermet essentially comprise the mechanical dispersion of nickel oxide in stabilized zirconium oxide, followed by the reduction of the nickel oxide to metallic nickel, usually during the anodic activation process with gaseous hydrogen at high
10 temperatures.

According to US patent 3,300,344, mixed zirconium and yttrium oxides (zirconia-yttria), obtained by removal of the solvent and calcination from an aqueous solution, are mould shaped with the addition of nickel oxide and coal in
15 powder form and the nickel oxide is then reduced to metallic nickel as a consequence of the high temperature coal.

Furthermore, the article "Morphology and Electrochemistry of Porous Nickel/Zirconia Cermets", (Proceedings of the First International Symposium on Solid Oxide Fuel
20 Cells, S.C. Singhal, Ed. 1989, pages 90-98) describes the reduction with hydrogen of a mixture of sintered powders obtained by co-grinding nickel oxide and stabilized zirconium oxide in a ball mill.

Other known techniques are those based on C.V.D.
25 (Chemical Vapour Deposition) and P.S. (Plasma Spraying),

described, for example by H. Arai in International Symposium on SOFC, November 13-14, 1989, Nagoya, Japan.

The nickel cermets obtained by means of the processes of the known art do not obtain completely satisfactory performances and do not have the necessary flexibility for
5 providing an optimum response to the various demands arising in their application in fuel cells.

One of the disadvantages which has not yet been overcome derives from the use of nickel oxide powders in the
10 normal preparation processes of anodic components. It has in fact been found that nickel oxide is a poisonous and carcinogenic material, which is dangerous for the environment and human organism, whereas the corresponding metallic nickel powders have a much lower danger threshold. The al-
15 most inevitable presence of nickel powders in working environments and in the preparation of electrodes for SOFC is the cause of serious preoccupation and is one of the reasons for limiting the commercial development of this type of SOFC, in other aspects extremely convenient and effi-
20 cient.

With respect to the above C.V.D. and P.S. techniques, there are, however, problems relating to both the quality of the material obtained, and to difficulties connected with the practical application of the techniques themselves
25 in the construction of medium and high power cells, includ-

ing their high cost, when compared with normal application techniques of electrode layers such as screen printing and airborne spraying.

Under another profile, the traditional preparation
5 techniques of nickel-based cermets are not particularly flexible when other elements are to be introduced together with the nickel, which are capable of conferring to the anode, in reduced form, in the metallic state, or in oxide form with particular dispersions and morphology, other
10 properties, such as, for example, a greater dimensional stability and mechanical resistance, promotion of the dispersion and reactive efficiency of the nickel towards the anodic gas, the capacity of activating the reforming of natural gas, resistance to micro-pollutants in food, and
15 others. With the traditional techniques, this has been achieved, for example, by mixing and sintering different types of oxides and reducing the solid thus obtained. In this way, however, a satisfactory homogeneity of the product is not obtained and the expected improvements are often
20 not observed.

Another problem which arises in the use in SOFC of anodes based on nickel cermets is the establishment of phenomena relating to the enlargement of the nickel grains with a progressive decrease in the catalytic activity. Experience in the use of nickel powders for the production of
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anodes for MCFC (molten carbonate fuel cells) shows that particular nickel alloys allow their creep resistance properties to be modulated and, in general, high temperature the mechanical stability: nickel alloys with chromium (5-
5 10% w) have higher creep resistance properties and high temperature mechanical stability as also nickel alloys with aluminum (5% w). It is possible that the use of particular alloys reduces the tendency of the nickel granules contained in the anodes to become enlarged, following long
10 functioning times at a high temperature.

The above drawbacks cannot even be solved by directly using compressed and shaped metallic nickel powders in a mixture with the ceramic material, as in this case a material is obtained with a dispersion which is not sufficiently
15 homogeneously and which does not have a satisfactory activity.

In spite of the continuous and rapid technological development in the field, there are still numerous problems to be solved in reply to the requests for improvement on
20 the part of industries and the market.

The Applicant has now found a new method for the preparation of nickel-based cermets, which is simpler and more convenient with respect to what is known so far, which represents considerable technical progress both in terms of
25 safety and also flexibility and the final properties of the

product obtained.

A first object of the present invention therefore relates to a method for the production of a ceramic-metallic composition (cermet) consisting of at least 70%, preferably
5 at least 85%, by weight of a solid material comprising, in a mixture, from 35 to 70% by weight of a metallic nickel phase and from 65 to 30% by weight of at least one oxide selected from oxides of transition metals and lanthanides, comprising the following steps in succession:

- 10 i) preparing a mixture of powders substantially free of nickel oxide, comprising metallic nickel and at least one oxide different from nickel oxide, selected from the oxides of transition metals and lanthanides;
- ii) laying said mixture of powders on a suitable surface,
15 in the form of a layer having a thickness ranging from 2 to 1500 μm , preferably from 10 to 650 μm , more preferably from 20 to 100 μm ;
- iii) heating said layer under oxidative conditions until reaching the desired sintering degree.

20 Other objects of the present invention will appear evident from the following description and claims.

The term powder, as used in the present description and claims with reference to metals or metal oxides, refers to a particulate having a particle-size which is such that
25 at least 90% by weight of the particles have a diameter

ranging from 0.5 to 500 μm .

According to a preferred aspect, the nickel cermet, obtained with the method of the present invention, consists of 35 to 70% by weight of a metallic nickel phase and from 5 65 to 30% by weight of a zirconium oxide (zirconia) phase, stabilized in cubic form by 3 to 15 moles, more preferably from 5 to 10 moles, of yttrium oxide (yttria) for every 100 moles of zirconium oxide, the two phases, upon X-ray diffractometry, being distinct and homogeneously distributed.

10 According to the method of the present invention, in step (i), a mixture of metallic nickel in powder form is prepared with at least one oxide of a transition metal or of the group of lanthanides. In step (i), the nickel and oxide (of a different transition metal) powders are mixed 15 with each other as homogeneously as possible, in such quantities as to respect the desired proportions in the final cermet.

The metallic nickel in powder form preferably has a particle-size which is such that d_{50} (mesh width of the 20 sieve which allows the passage of 50% by weight of the powder) ranges from 1 to 5 μm , more preferably from 2 to 3 μm . Powders with a bi- or poly-modal distribution, or having a filamentous structure (microfibres) or mixtures of said powders can also be used in accordance with said step (i). 25 These powders can be obtained by the grinding of metallic

nickel in an inert atmosphere, by means of processes and equipment well known in the art. Nickel powders with the above particle-sizes are also commercially available, for example under the trade-names of PRAXAIR®, INCO 255®. Although metallic nickel powders are subject to precise safety regulations for their, they do not have the characteristics of environmental and health risk as shown, on the contrary, by nickel oxide powders.

Suitable metal oxides for the formation of the mixture of powders according to step (i) are porous oxides or mixtures of oxides having the function of an electrolyte under the functioning conditions of an SOFC. Said lanthanide oxides or oxides of transition metals exert, in the final form of the cermet, a supporting and ion transporting function, making the anode more stable with time and allowing the maximum dispersion of the nickel to increase the contact with the reducing gas (usually hydrogen). Oxides suitable for this purpose have been developed for some time and are widely described in technical literature in the field. Typical, non-limiting examples are oxides of Bi, Sr, Zr, Y, Ce, Ga, Sc, Mn, La, Ca, Pr, Yb, Nd, Sm and mixtures thereof. In particular, excellent results can be obtained mixed oxides of Zr and Y (zirconia-yttrium), especially in an atomic ratio of 92/8 (commercial product also called 8YSZ), Ce and Ga (cerium-gadolinia), Zr and Ca (zirconia-

calcia), and in general oxides and mixed oxides known in the specific field as SOFC electrolytes.

The above powders of oxides preferably have an average diameter ranging from 8 μm to 20 μm and a relatively narrow
5 size distribution of the granules.

The preparation of the mixture of powders according to step (i) can be effected according to any of the known methods suitable for the purpose. Among these, the most common method is simple mixing of the preformed powders in
10 a suitable container. It is also possible to carry out a co-grinding of the powders to improve the homogeneity of the mixture thus obtained. The co-grinding is effected, according to the art, in suitable mortars, jars, or other closed containers, with the help of steel balls and a suitable
15 vibrating device. A further technique consists of co-grinding the components with rougher shapes and dimensions, in suitable mills, to obtain a powder having the desired particle-size.

Step (ii) of the method according to the present invention consists in the preparation, with any suitable apparatus and method, of a layer of the mixture obtained in
20 step (i) having the desired thickness. This layer can be laid on a suitable carrier which can advantageously also consist of a layer of a suitable SOFC electrolyte, normally
25 having a thickness ranging from 200 to 800 μm , preferably

from 300 to 600 μm .

The conformation of the layer obtained according to step (ii) is not critical but can vary according to the circumstances and final use of the cermet produced. Examples of geometries suitable for use in fuel cells having different forms are, for example, simple flat geometry, obtained for example with tape casting technologies, or a cylindrical geometry, produced for example by the slurry coating of a suspension in an aqueous solution of methyl cellulose.

One of the known techniques which is most suitable for the purpose is screen printing, adapted to the circumstances of the specific case. Before the formation of the layer in step (ii), suitable organic components are normally added to the mixture of powders obtained in step (i), suitable for forming a paste having the desired viscosity and consistence, with thixotropic properties. Components of this kind are waxes or organic oils, either liquid or with a creamy consistency at room temperature, or solutions of cellulose derivatives, which undergo decomposition and oxidation in the subsequent phase (iii) of the present method without substantially leaving traces or residues in the cermet obtained at the end.

It may also be convenient, according to what is known in the art, to add a granular solid to the pasty mixture,

which is decomposable either thermally or under oxidative conditions, such as, for example, graphite powder with dimensions in the order of tens of μm , in order to favour the formation of a porous structure in the end-product.

5 The layer of powders (or paste obtained therewith) normally has a thickness ranging from 50 to 1500 μm , and preferably from 200 to 1000 μm for supporting anodes and from 50 to 300 μm for supported anodes.

According to a particular embodiment of the present
10 invention, said anodic layer is not obtained separately from the other essential layers of the cell, but is shaped into the desired form, with at least one surface in contact with an electrolyte layer or with a precursor thereof, for example a serigraphic paste of the type mentioned above.
15 The electrolyte is selected from any of the materials suitable for the purpose, preferably one of the above oxides or mixtures of oxides of a transition metal or lanthanide, more preferably the same electrolyte oxide used in a mixture with the nickel powder of step (i). The precursor layers thus assembled are then subjected to treatment according to the subsequent step (iii).
20

 The heating under oxidizing conditions in step (iii) of the layer of powders obtained in step (ii), is carried out at a temperature and for a duration which are sufficient for obtaining the desired sintering degree of the
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cermet (or whole cell element if already prepared together with the cermet forming the anode), to form a solid having the desired consistency consisting of particles of oxide, preferably YSZ, with high temperature ion conductor characteristics, covered with nickel oxide. The heating conditions are preferably selected from those normally used in obtaining SOFC anodic layers. In particular, suitable sintering temperatures generally range from 900 to 1600°C, more preferably from 1100 to 1500°C, and the times can vary from a few minutes to several hours. According to a particularly preferred embodiment, with zirconia-based oxides, it is preferable to operate at temperatures in the order of 1100-1300°C for a time ranging from 30 minutes to 4 hours. These conditions can also significantly vary depending on the pressure used and physico-chemical characteristics of the material, according to what is known to experts in the field.

The oxidizing environment can consist of oxygen, air or oxygen-enriched air. Operating under these conditions, in addition to making the layer of powders self-consistent, there is also the formation of the oxides of the metals present (Ni and possible additional metals, for example Cu, Cr, Co, Rh, Ru, Al). In this way, a nickel oxide or a mixture of this oxide with other possible oxides of said additional metals, is obtained, which proves to be surprisingly

effective both in the normal use of the cermet as anode in a SOFC, and also in the catalysis of the contemporaneous reforming in the case of feeding with hydrocarbons. Even if this does not refer to any particular theory or model, it is felt that the best performances of the cermet, according to the present invention, can be attributed to an unusual arrangement and morphology of the additional metal on the nickel particle.

Said step (iii) is preferably preceded by an optional pre-sintering process at a temperature close to the sintering value, at which said mixtures of powders are transformed into an aggregate material which is such that it does not release powders into the environment. This aggregation process is different and precedes the sintering process in which, with the possible help of high pressures, micro-fusions are formed on the surface of the granules. In particular, said temperature close to the sintering value is conveniently selected from 50 to 300°C lower than the minimum temperature at which a certain mixture of powders, under the pre-selected pressure conditions, begins to sinter. For many of the mixtures of powders prepared according to step (i) and (ii) of the present invention, said temperature is normally higher than 800°C, preferably ranging from 1000 to 1300°C.

According to a particularly preferred aspect of the

present invention, all the metallic nickel present in the mixture of powders is essentially transformed into oxide during said step (iii), so that at the end, the content of metallic nickel possibly remaining in the sintered layer is
5 lower than 0.5% by weight, preferably lower than 0.1% by weight.

In the practical embodiment of step (iii), according to the usual sintering techniques, the layer of powders is subjected to progressive heating following a pre-
10 established profile, until the effective pre-sintering and/or sintering temperature is reached, in order to avoid the arising of defects or distortions due to a sudden heating up to temperatures in the order of 1000°C.

The porous solid (or sintered) layer, obtained at the
15 end of said step (iii) is normally subjected to a further optional treatment (iv) with hydrogen, to reduce the nickel oxide to metallic nickel and thus obtain the desired product ready for use in an SOFC. Said step (iv) is preferably carried out after installation of the sintered layer in the
20 anodic structure of a fuel cell, as an activation step by the passage of hydrogen at a high temperature.

In particular, the reduction is carried out by putting the solid in contact with hydrogen or with a gas containing hydrogen, for example H₂/Ar mixtures, operating at temperatures ranging from 600 to 1000°C and H₂ pressures ranging
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from 50 to 500 Kpa, in order to obtain the complete or substantially complete reduction of the nickel oxide (NiO) to metallic Ni. During the reduction step, any other possible reducible oxides, such as, for example, CuO or CoO, present
5 in the solid layer are transformed into the corresponding metal in close contact with the nickel, obtaining an improved efficacy in the subsequent uses as a multifunctional cell anode.

Convenient reduction times are in the order of 5 to 48
10 hours, preferably from 10 to 30 hours, depending on the thickness of the anodic layer. In a particular embodiment, the reduction mixture has a hydrogen content which increases with time until reaching the pre-established partial pressure value.

15 The ceramic-metallic composition (nickel cermet) thus obtained has a porous structure with a porosity (pore volume/apparent volume of the solid, measured by means of a mercury porosimeter) ranging from 30 to 80%, preferably from 30 to 50% for thin anodes and from 40 to 70% for supported
20 anodes, in which the surface portion of the oxide covered by nickel generally ranges from 4 to 30% or even more).

According to the method of the present invention, nickel oxide powders are not used as starting material and
25 neither are these powders produced or made accessible to

operators during any of the steps of the embodiment of the method, as the nickel oxide produced under the oxidative conditions of step (iii) is already in a stratified and structurally stable conformation which does not produce any powder dispersion in the surrounding environment. The present method thus proves to be significantly advantageous and enhanced with respect to the known art, also in terms of a lower impact relating to health and environment.

It has also been found that, with the present method, it is possible to prepare cermets containing, in addition to nickel, at least another metal M selected from transition metals, particularly metals of groups 8, 9, 10 and 11 of the periodic table of elements. Said metal M, added in metallic form or as an oxide different from that forming the electrolytic oxide, gives the cermet additional catalytic activities and is distributed, when metal fine powder is used as starting material, with an advantageous conformation with respect to the nickel particles, i.e. irregularly arranged in microlayers on said particles.

The metal M is particularly selected from transition metals with a redox or hydrogenating capacity, such as Cu, Co, Fe, Rh, Ru, Pt and Pd.

In accordance with this further aspect of the present invention, the nickel in powder form can be premixed (for example by co-grinding) with the metal M, preferably in the

form of a metallic powder, for example Ni and Al, Ni and Cu, Ni and Rh, Ni and Co, Ni and Ru, before carrying out step (i) of the claimed process. Nickel is in fact suitable for the preparation of alloys with numerous metals, also by mechanical alloying (for example by co-grinding in a friction mill) which does not require mixing of the two metals in the molten state and subsequent grinding, but allows, in the metallic precursor phase, in step (i), mixtures of metals to be introduced in a heterogeneous particulate, but in close contact with each other, capable of producing, in the final cermet, morphologies which cannot be obtained with the usual metallic alloys. Furthermore, it is thus possible to closely combine metals which are not miscible with each other in alloys. The use of alloyed nickel powders with suitable promoters could therefore lead the way to the production of SOFC anodes capable of providing higher performances than those of the traditional anodes. It is thus possible to obtain composite (alloyed) metallic powders based on nickel and one or more other metals capable of exerting coadjuvant functions during the use of the cermet.

The quantity of metal M added to the mixture of step (i) is selected on the basis of the desired application. Suitable amounts of metal M may be ranging in a quantity from 1 to 80%, preferably from 2 to 40%, even more preferably from 2 to 15%, by weight with respect to the nickel.

Said further metal M can also be added according to the tape-casting technique, in which the metal M, the nickel in powder form and the electrolyte oxide (for example YSZ) are suspended in an aqueous solution of methyl
5 cellulose to obtain a paste, which is then laid in a layer having the desired shape and thickness and subsequently calcined and sintered according to step (iii).

Said tape-casting technique is, more generally, among those which can be used for obtaining compositions according to the present invention, in a planar form suitable for
10 the production of cells with supporting anodes (normally called anode-supported SOFC), in which the thickness of the anodic layer preferably ranges from 200 to 1000 μm , more preferably from 400 to 800 μm , whereas the electrolyte
15 layer is much thinner than that of the traditional SOFC, and normally ranges from 10 to 50 μm . In a preferred embodiment, the anode of these cells is structured in a supporting layer of the type specified above and a further thin anodic layer (10-50 μm), subsequently laid on the
20 first.

The method according to the present invention advantageously allows said cells with a supporting anode to be obtained, with lesser risks of causing fractures of the planar layers, as a result of tensions caused by the different
25 shrinkage coefficient of the materials during the sintering

step.

It has also been found that when the method according to the present invention is used for the preparation of porous anodic supports by means of tape-casting, it has the further advantage of a limited environmental impact as it is possible to prepare the suspension by casting in an aqueous liquid medium, avoiding the use of solvents or organic dispersing agents, potentially harmful if dispersed in the atmosphere.

Alternatively, before calcination, it is possible to lyophilize the layer for a better fixing of its shape.

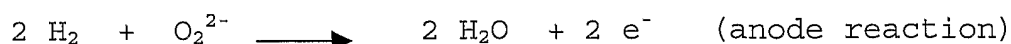
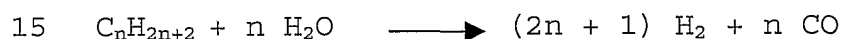
The present method however also comprises the introduction, in step (i) or also in the preparation of the composition of step (ii), of the additional metal M in a different form from the metallic state, for example in the form of an oxide (for example CuO, CoO, Cr₂O₃), or a suitable salt (thermally decomposable, for example nitrate) by means of impregnation.

In accordance with what is specified above, when M forms metallic oxides which can be reduced with hydrogen, multi-metallic cermets are obtained, after reduction according to step (iv), which form a further object of the present invention, and are characterized by a particular arrangement of the additional metal, which is stratified on the surface of the nickel granules, in areas or patches

having a fine thickness and high surface, whereas the structure observed when the known procedures are used, starting from oxides, consists of micro-granules of said metal adjacent to or dispersed on the nickel granule.

5 A particular embodiment of the present invention relates to the preparation of such cermets of Ni containing additional metals M suitable for the contemporaneous steam or dry reforming of light hydrocarbons on a SOFC anode.

As it is known to the skilled people, such metals like
10 Pt, Ir and Cu can advantageously be added to nickel in the SOFC anode in order to carry out the steam reforming reaction of hydrocarbons, thus producing hydrogen ready for the anodic oxydation reaction, according to the following, non-limiting scheme:



However, several side reaction are possible at such temperature conditions as those reached in a SOFC, particularly the decomposition of hydrocarbons to graphitic carbon, catalyzed by Ni (so called "coking", because coke is finally deposited on the anode). Graphitic carbon has two main detrimental effects: it decreases the available metal surface for the anodic reactions, and it forms alloys with
25 Nickel, thus impairing the mechanical properties of the

material.

The addition of such metals as Cu, Rh, Ir or Pt to the anodic nickel cermet composition strongly decrease the formation of coke, most probably because the metals inhibit
5 the adsorption of carbon within nickel and promote the hydrocarbon oxydation by steam. Copper is preferred because of its much lower cost with respect to other noble metals.

The method of the present invention allows the preparation of excellent compositions of Ni and additional copper,
10 per, not only because no nickel oxide powder is used, but also because, in the preferred case of alligation of the two metals in step (i), it produces a very good dispersion of copper on the surface of the nickel granules.

For the aim of improving the steam reforming reaction
15 the metal Cu is preferably added to Ni in a quantity ranging from 2 to 20%, preferably from 5 to 10%, by weight with respect to the Ni.

A SOFC operated in such a way as to have also steam reforming reaction in its anodic portion, is usually fed
20 with a gaseous stream containing hydrocarbons, particularly natural gas or other mixture of methane with up to 30% by volume of higher hydrocarbons from ethane to hexane, and steam, in an amount at least sufficient to complete the foregoing reactions.

25 Preferably, steam is used in a volume ratio from 1/1

to 4/1 with respect to the hydrocarbons. Optimum operating conditions and details relating to SOFC anodic process including hydrocarbon reforming are well known in the art and available in a large number of publications and treaties.

5 An even further aspect of the present invention relates to the use of the nickel cermet described above as an anodic material (with the possibility of reforming) for solid oxide fuel cells (SOFC).

10 In particular, this type of anode can be obtained by depositing, according to step (ii) above, for example by means of the techniques described, screen printing, plasma spraying, the nickel cermet of the present invention on a solid element consisting of an electrolyte of zirconium oxide stabilized with yttrium oxide, or another suitable
15 electrolyte according to the known art, like ceria stabilized with gadolinia. According to a particular embodiment, step (iv) for the reduction of the nickel oxide to metallic nickel can take place "in situ", after the preparation of the cell structure: anode/electrolyte/cathode, and option-
20 ally its positioning in the stack.

 These solid oxide fuel cell comprising an anode made with the ceramic metallic composition of the present invention are conveniently used in a process for producing electric power.

25 The Applicant has further found that an improvement is

achieved, in terms of efficiency, start-up and durability of power production, when the anode of said SOFC cell comprises a bimetallic composition of nickel and a redox metal like Cu, Pt, Rh, Ir, Pd, particularly in the presence of a contemporaneous steam-reforming reaction in the anodic section of the cell, wherein a gas mixture of steam and a hydrocarbon is fed to. Typical fed hydrocarbon is selected from methane, natural gas and a mixture of methane and light hydrocarbons.

10 The following examples are provided for a further illustration of the invention but should in no way be considered as limiting the scope of the invention itself.

Examples

Example 1: Preparation of an anodic layer for SOFC cells starting from metallic Ni and YSZ.

Preparation of the mixture of powders

A mixture is prepared, consisting of 42 g (35% by weight) of Zirconia ceramic material stabilized with Yttria (8-YSZ, TOSOH product) and 78 g (65% by weight) of metallic nickel (INCO 255 product), both in powder form.

The particle-size of the ceramic powder is such that at least 95% of the granules has dimensions within the range of 5 to 10 microns; the particle-size of the nickel powder ranges from 1 to 2 microns.

25 The mixture is put in a 250 ml zirconia jar and is

suspended in 100 ml of deionized water. 7 zirconia balls having a diameter of 2 cm are added to the jar, and grinding is effected in a vibration mill for 24 hours.

At the end, the water is evaporated by means of a lyophilization process and about 120 g of a homogeneously distributed solid mixture is obtained.

Preparation of the anodic layer with a screen printing method

60 g of a carrier having suitable rheological properties for the preparation of a serigraphic ink, are added to the above solid mixture. The carrier consists of a solution of ethyl cellulose (14% by weight) in α -terpineol, having a viscosity of 45 mPa. The mixture is kept under stirring for 48 hours in order to make it homogeneous and passed over a zirconia roll paste mixer to finely disperse the powder granules.

The serigraphic ink thus obtained is deposited by screen printing on an electrolytic membrane consisting of YSZ (KERAFO[®]L product), having a thickness of about 160 μ m and dimensions of 5 x 5 cm². The serigraphic halftone screen used is 250 mesh made of steel. By passage of the doctor blade on the halftone screen, the ink is deposited on the electrolytic membrane, the thickness of the layer deposited with a single passage of the doctor blade is about 10 μ m, a total of three passages are effected to ob-

tain the optimum thickness for the anodic layer of about 30 μm .

The electrolytic membrane with the anodic layer (semi-cell) is left for 15 minutes at room temperature to allow a leveling of the layer itself, and is then put in an oven at 120°C to remove the α -terpineol, thus allowing the semicell to be handled for the subsequent deposition of the cathodic layer effected with the same procedure on the side of the electrolyte remaining free. The cathodic layer consists of a layer of LSM (lanthanum manganite and strontium, Nextech product).

Preparation of the semi-sintered product.

At the end of the deposition phase of the electrodes, the complete cell is put into an oven for the co-sintering in air of the electrodes.

The sintering cycle is indicated in Table 1 below:

Step	Temperature (°C)	Heating rate (°C/h)	Stoppage (h)
1	120	50	-
2	170	10	2
3	210	5	2
4	250	5	2
5	440	20	-
6	800	50	3
7	1200	120	2
8	80	120	-

The anodic layer after the sintering cycle in air consists of YSZ and NiO with a porosity ranging from 30% to 40%.

The nickel oxide is then reduced to metallic nickel using a reducing gas (hydrogen) directly in the housing of the SOFC cell (cell-holder) during the electric characterization phase.

Electric characterization

The cell-holder consists of two ceramic shells between which the cell is inserted. A nickel net (which acts as anodic current collector) is applied on the lower shell (anodic section) and subsequently the SOFC cell. A gold washer, situated between the shell and cell, prevents the discharge of hydrogen from the anodic section.

The upper shell of the cell-holder equipped with a platinum net which acts as cathodic current collector, is then placed on top.

At the end of the assembly operation, the cell-holder is inserted in the oven where reduction is effected. A stream containing Ar is initially sent, and its hydrogen content is gradually increased until it completely replaces the Ar over a period of 3 hours. The temperature is brought to 800°C and hydrogen is maintained for a further 3 hours. The oven is then cooled and the Ar content is increased again in the gas stream until the substantial elimination

of the hydrogen.

After the reduction of the functional anodic layer, the cell was subjected to electric characterization. The operating conditions were as follows:

5 Operating temperature: 950°C

 Anodic gas: hydrogen, 0.5 litres/minute

 Cathodic gas: air, 0.5 litres/minute

 The determination of the voltage/current curve was effected by increasing the density of the current supplied by the cell and monitoring the voltage. The same measurement was effected on a traditional-type cell, obtained with the same procedure described above, but using an equivalent quantity of NiO in powder form in the place of metallic Ni in the first step. The results summarized in Table 2 below
15 were obtained.

CURRENT (mA/cm ²)	CELL VOLTAGE (mV)	
	EXAMPLE 1	TRADITIONAL
0	1180	1180
25	1120	1100
50	1060	1050
100	965	970
150	895	915
205	814	846

20 Table 2

25 The measurement indicates that, with the same operat-

ing conditions, the performances for both types of cell are substantially equivalent within the experimental accuracy range.

Example 2: preparation of an anodic layer (cermet) for SOFC cells starting from metallic nickel and Ceria stabilized with Gadolinia (CGO).

Preparation of the mixture of powders

A mixture is prepared, consisting of 50 g of Ceria ceramic material stabilized with Gadolinia (CGO, 40% by weight, Rhodia product) and 72 g of metallic nickel (60% by weight, INCO 255 product), both in powder form.

The particle-size of the ceramic powder is such that at least 95% of the granules has dimensions within the range of 1 to 2 μm ; the particle-size of the nickel powder equally ranges from 1 to 2 μm .

The mixture is put in a 250 ml zirconia jar and is suspended in 100 ml of deionized water. 7 zirconia balls having a diameter of 2 cm are added to the jar and grinding is effected for 24 hours in a vibration mill.

At the end, the water is evaporated by means of a lyophilization process and about 121 g of a homogeneously distributed solid mixture are obtained.

Preparation of the anodic layer with the screen printing method

Exactly the same procedure is adopted for the prepara-

tion and sintering of the anodic layer as described in Example 1, obtaining at the end a compact and mechanically resistant ceramic layer, having an average thickness of about 30 μm , consisting of Ni oxide and CGO in a weight ratio of 60/40.

Example 3: Methane steam-reforming test

The ceramic-metallic materials (or their precursors) prepared according to the previous Examples 1 and 2, were evaluated in methane steam-reforming tests under the normal operating conditions of an SOFC cell. For this purpose, the approximately 500 mg sample of each material, reduced to granular particulate (average dimension about 0.3 mm) was introduced into a quartz tubular reactor with a diameter of 13 mm, compressed between two double-layers, about 40 mm thick, of inert porous material, each composed of a layer of quartz grains and a layer of fiberglass. It was then reduced with hydrogen, operating at 600°C, with an analogous procedure to that described in Example 1 above. All traces of hydrogen are eliminated by passing helium until the disappearance of the characteristic chromatographic signal.

A mixture consisting of water vapour and methane is then fed, in a molar ratio $\text{H}_2\text{O}/\text{CH}_4 = 2.27$. The WHSV space velocity is set at 2.6 h^{-1} . The reaction products leaving the tubular reactor are analyzed by means of gaschromatography. The temperature of the reactor is maintained at

850°C. Under these conditions, the activity of the samples obtained according to the previous examples 1 and 2 reached the following stable methane conversion values after 30 hours of running:

5 Example 1 Ni/YSZ stable conversion = 80%

 Example 2 Ni/CGO stable conversion = 82%

 These values remain almost constant until at least up to 80 hours of running.

 For comparative purposes, a sample of Ni/YSZ obtained
10 with the traditional method starting from powder oxides, was tested, obtaining a stable conversion after 30 hours of 90%, slightly higher, but substantially comparable with that of the samples according to the present invention.

 The method of the present invention therefore allow
15 ceramic-metallic compositions to be obtained, under safer conditions and with a lower environmental impact, having electric and catalytic properties suitable for use in the preparation of SOFC, essentially similar to those of the analogous materials obtained from NiO powders.

20 **Example 4:** Ni-Cu bimetallic anodic composition

 A ceramic-metallic composition comprising nickel and copper was prepared with a method analogous to that described in Example 1.

 95 g of nickel in powder form (INCO 255) and 5 g of
25 copper in powder form (Aldrich product) were mechanically

mixed and subsequently placed in a friction mill for 72 h. At the end, a Ni powder alloyed with Cu was obtained, which under an electronic microscope (EDS probe) revealed a homogeneous arrangement of copper on the nickel grains.

5 65 g of the alloyed powder prepared as described above were mixed with 35 g of 8-YSZ (TOSOH product) and the mixture was treated with the same method described in Example 1 above, until an anodic layer having a thickness of 30 μm was obtained, after calcination.

10 **Example 5: Methane steam-reforming test**

 The ceramic-metallic material, prepared according to the previous Example 4, was evaluated in methane steam-reforming test by using the same laboratory reactor as described in previous example 3. Approximately 500 mg of each
15 material, scraped from the anodic layer, were pressed to a tablet and then reduced to granular particulate by grinding (average dimension about 0.3 mm). The sample so obtained was introduced into the tubular reactor. It was then reduced with hydrogen, operating at 600°C, with an analogous
20 procedure to that described in Example 1 above. All traces of hydrogen are eliminated by passing helium until the disappearance of the characteristic chromatographic signal.

 A mixture consisting of steam and a hydrocarbon composition containing, by volume, 87% methane, 10% ethane and
25 3% propane, with a ratio $\text{H}_2\text{O}/\text{C}_{(\text{tot})} = 2.0$, was fed to the re-

actor at a WHSV space velocity of 2.1 h^{-1} . The reaction products leaving the tubular reactor are analyzed by means of gaschromatography. The temperature of the reactor is maintained at 800°C .

5 An initial carbon conversion of 70% was observed, which turned to about 80% after 200 hours running and remained stable to such value up to 500 hours, when the experiment was interrupted. The carbon balance between the feed and product streams has shown that essentially no
10 solid carbon remained in the reactor.

 The cermet composition obtained from the alloyed metals, containing only 5% of copper, has shown essentially no induction time at the start time of the experiment, and no deactivation or solid carbon deposition after 500 hours
15 running.

 The new bimetallic compositions according to the present invention reveal to be quite suitable for the preparation of fuel cells capable of excellent performance when operated under steam-reforming conditions.

20 **Example 6:** preparation of anode-supported SOFC structures
 Preparation of the Ni/YSZ porous anodic carrier

 An aqueous suspension was prepared, having the following composition:

Nickel (metallic phase)	78 g (INCO 255)
25 8-YSZ (ceramic phase)	42 g (Lonza)

Metal/ceramic ratio 65/35% by weight

The powders were suspended in an aqueous solution of methyl cellulose (Fluka, 63000 cps) at 2.5% by weight and the suspension obtained (slurry) was homogenized by mechanical stirring for 2 hours.

After the mixing, the slurry is deaerated for 24 hours by continuous rotation of the container on rolls. Immediately before the casting, the slurry is poured into the basin of a sliding trolley (doctor blade). The trolley has two blades whose distance from the casting plane can be regulated by means of micrometric screws.

The width of the trolley basin automatically determines the width of the tape. The rate of the trolley was regulated by an electric moving system and was established at 0.2 m/min. The solution spread was dried at room temperature for 24 hours. The tape thus obtained was cut so as to obtain test samples having dimensions of about 6 x 6 cm² and subjected to a pressure of about 150 kg/cm² for ten minutes so as to obtain its mechanical settlement. After pressing, the tape is subjected to a pre-sintering thermal cycle in air which comprises a first phase up to 600°C at a rate of 30°C/h to remove the organic phase, followed by a rise of 20°C/h up to the maximum temperature of 1200°C. During this phase, the nickel is oxidized, already at about 750°C, and the end-product is therefore a porous carrier

consisting of YSZ and NiO.

A further anodic layer having a thickness of about 20 μm was deposited on the pre-sintered anodic carrier, following the procedure indicated in Example 1. After drying
5 the porous carrier with the anodic layer at 120°C, an electrolyte layer was deposited by screen printing a paste consisting of 150 g of 8-YSZ and 53 g of the same ligand used in Example 1 (ethyl cellulose at 14% by weight in α -terpineol). After drying at 120°C, the semicell thus pre-
10 pared was sintered at 1400°C according to a thermal cycle which comprises a first phase up to 600°C at a rate of 30°C/h to remove the organic phase, following by a rise of 20°C/h up to the maximum temperature of 1400°C. In this way, a semicell was obtained, consisting of a po-
15 rous/anode/electrolyte carrier, followed by the deposition and sintering at 1200°C of the cathodic layer as described in Example 1 to complete the preparation of the cell.

The cell has a structure essentially without fractures, demonstrating the advantageous behaviour with
20 shrinkage in the sintering phase.

The "anode-supported" SOFC structure was subjected to electric characterization according to the method described in Example 1. The reduction phase (activation of the porous carrier and anode) was effected at 800°C in an Ar/H₂ mix-
25 ture, progressively increasing the hydrogen concentration.

After reduction, the SOFC was characterized according to the following procedure:

Operating temperature: 800°C

Anodic gas: hydrogen, 0.5 litres/minute

5 Cathodic gas: air, 0.5 litres/minute

The determination of the voltage/current curve was effected by increasing the density of the current supplied by the cell and monitoring the voltage. The results obtained are summarized in Table 3 below.

10 Table 3

CURRENT (mA/cm ²)	VOLTAGE (mV)
0	1050
25	900
50	850
100	600
150	550
205	480

20

CLAIMS

1. A method for the production of a ceramic-metallic composition (cermet) consisting of at least 70% by weight of a solid material comprising from 35 to 70% by weight of a metallic nickel phase and from 65 to 30%
5 by weight of at least one oxide selected from oxides of transition metals and lanthanides, comprising the following steps in succession:
 - i) preparing a mixture of powders essentially free
10 of nickel oxide, comprising metallic nickel and at least one oxide selected from oxides of transition metals and lanthanides;
 - ii) laying said mixture of powders on a suitable surface, in the form of a layer having a thickness ranging
15 from 2 to 1500 μm ;
 - iii) heating said layer under oxidative conditions until obtaining the desired sintering degree of the powders.
2. The method according to claim 1, wherein, in said step
20 (iii), essentially all of the metallic nickel present in the mixture of powders is transformed into oxide.
3. The method according to claim 1 or 2, wherein the content of metallic nickel in the layer at the end of step (iii) is less than 0.5% by weight.
- 25 4. The method according to any of claims 2 or 3, compris-

ing a further step (iv) wherein the nickel oxide is reduced to metallic nickel by means of hydrogen.

5. The method according to the previous claim 4, wherein said reduction is carried out with hydrogen pressures ranging from 50 to 500 KPa.
6. The method according to any of the previous claims from 1 to 5, wherein said composition consists of at least 85% by weight of said solid material.
7. The method according to any of the previous claims from 1 to 5, wherein, in said step (i), the porous oxides or mixtures of oxides is selected among the oxides that can act as an electrolyte under the functioning conditions of an SOFC.
8. The method according to claim 7, wherein said oxides of lanthanides or transition metals are selected from oxides of Bi, Sr, Zr, Y, Ce, Ga, Sc, Mn, La, Ca, Pr, Yb, Nd, Sm and mixtures thereof, preferably mixtures of Zr and Y or mixtures of Ce and Ga oxides.
9. The method according to any of the previous claims from 1 to 8, wherein, in said step (ii), the layer of powders (or the paste obtained therewith) has a thickness ranging from 200 to 1000 μm for supporting anodes and from 50 to 300 μm for supported anodes.
10. The method according to any of the previous claims from 1 to 9, wherein, said step (ii) is carried out by

laying said layer with at least one surface in contact with an electrolyte layer or with a precursor thereof, as component of the anodic layer of an SOFC cell.

11. The method according to any of the previous claims
5 from 1 to 10, wherein, in said step (ii), the layer of powders is prepared by means of a screen printing, tape-casting or plasma spraying method.
12. The method according to any of the previous claims
10 from 1 to 11, wherein at least another metal M different from that forming the electrolyte oxide, is added to the metallic Ni, previously or during said step (i).
13. The method according to the previous claim 12, wherein
15 said metal M is selected from transition metals, particularly from metals of groups 8, 9, 10 and 11 of the periodic table of the elements.
14. The method according to any of the previous claims 12 or 13, wherein said metal M is selected from transition metals with a redox or hydrogenating capacity.
- 20 15. The method according to any of the previous claims from 12 to 14, wherein said metal is selected from the group consisting of Cu, Co, Fe, Rh, Ru, Pt and Pd, preferably Cu.
- 25 16. The method according to any of the previous claims from 12 to 15, wherein the amount of said metal M in

the cermet composition is comprised from 1 to 80% by weight, with respect to the nickel.

17. The method according to previous claim 16, wherein the amount of said metal M is comprised from 2 to 15% by weight, with respect to the nickel.
18. The method according to any of the previous claims from 12 to 17, wherein, in step (i), nickel and said metal M, are mechanically alloyed before the admixing of said oxide of transition metals or lanthanides.
- 10 19. The method according to any of the previous claims from 12 to 17, wherein nickel, said metal M, in metallic state or as an oxide, and said electrolyte oxide are mixed together and laid in a form of a layer according to the tape-casting technique.
- 15 20. The method according to any of the previous claims, wherein said step (iii) is carried out at temperatures ranging from 900 to 1700°C.
21. The method according to the previous claim 20, wherein, said step (iii) is carried out at an operating temperature ranging from 1200 to 1300°C for a time ranging from 10 minutes to 3 hours.
- 20 22. The method according to any of the previous claims, wherein said step (iii) is preceded by a pre-sintering step at a temperature selected from 50 to 300°C lower than the minimum temperature at which the mixture of
- 25

powders starts to sinter.

23. The method according to any of the previous claims, comprising a further grinding step to obtain a ceramic metallic composition in granular or powder form.
- 5 24. A ceramic metallic composition having a porous structure with a porosity (measured by means of a mercury porosimeter) ranging from 30 to 80%, wherein the surface portion of the oxide covered by nickel ranges from 4 to 30%, characterized in that it is obtained by
10 a method according to any of the previous claims from 1 to 23.
25. The composition according to the previous claim 24, comprising, in addition to nickel, a second metal M in the metallic state.
- 15 26. The composition according to the previous claim 25, wherein said metal M is selected from transition metals of groups 8, 9, 10 and 11 of the periodic table of elements.
27. The composition according to the previous claim 26,
20 wherein said metal M is copper.
28. The composition according to the previous claim 26, wherein the amount of said metal M is comprised between 1 and 80% by weight with respect to the amount of nickel.
- 25 29. The composition according to any of the previous

claims from 24 to 28, obtained in granular or powder form.

30. Use of the ceramic metallic composition according to any of the claims from 24 to 29, for the preparation
5 of the anodic layer of a solid oxide fuel cell.

31. A method for the preparation of anode-supported SOFC structures, comprising the preparation of a porous anodic carrier having a thickness ranging from 200 to 1500 μm , characterized in that said carrier is prepared in accordance with the method according to any
10 of the claims from 1 to 23.

32. The method according to claim 31, wherein a thin anodic layer and a thin electrolyte layer, preferably with a thickness ranging from 10 to 50 μm , co-sintered at 1300-1500°C, and a cathodic layer sintered at 1000-1200°C, are deposited on said porous carrier.
15

33. A process for producing electric power by mean of a solid oxide fuel cell, characterized in that the anode of said cell comprises a ceramic metallic composition according to any of the claims from 24 to 29.
20

34. The process according to the previous claim 33, further comprising a contemporaneous steam-reforming reaction, wherein a gas mixture of steam and a hydrocarbon is fed to the anode of the cell.

25 35. The process according to the previous claim 34,

wherein said anode comprises a bimetallic composition of nickel and copper.

36. The process according to any of the previous claims 34 and 35, wherein said hydrocarbon is selected from methane, natural gas and a mixture of methane and light hydrocarbons.