



(86) Date de dépôt PCT/PCT Filing Date: 2005/06/09
(87) Date publication PCT/PCT Publication Date: 2005/12/22
(45) Date de délivrance/Issue Date: 2011/05/17
(85) Entrée phase nationale/National Entry: 2006/12/08
(86) N° demande PCT/PCT Application No.: DK 2005/000379
(87) N° publication PCT/PCT Publication No.: 2005/122300
(30) Priorités/Priorities: 2004/06/10 (DK PA 2004 00904);
2005/02/02 (DK PA 2005 00159)

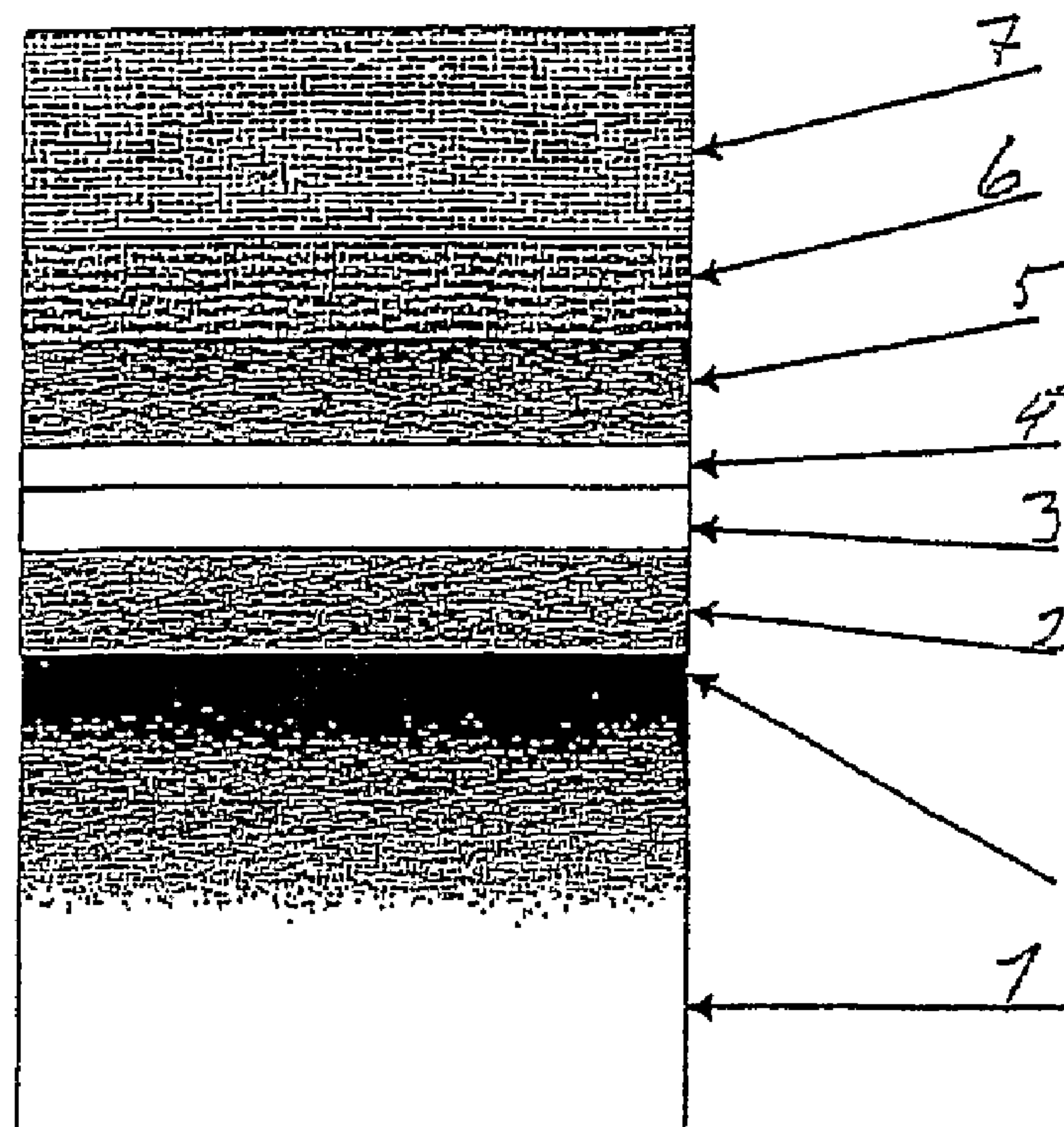
(51) Cl.Int./Int.Cl. *H01M 8/12* (2006.01),
H01M 4/86 (2006.01), *H01M 4/88* (2006.01),
H01M 4/90 (2006.01), *H01M 8/02* (2006.01)

(72) Inventeurs/Inventors:
LARSEN, PETER HALVOR, DK;
MOGENSEN, MOGENS BJERG, DK;
LINDEROTH, SOEREN, DK;
HANSEN, KENT KAMMER, DK;
WANG, WEIGUO, DK

(73) Propriétaire/Owner:
TECHNICAL UNIVERSITY OF DENMARK, DK

(74) Agent: BORDEN LADNER GERVAIS LLP

(54) Titre : PILE A COMBUSTIBLE A OXYDE SOLIDE
(54) Title: SOLID OXIDE FUEL CELL



(57) Abrégé/Abstract:

SOFC cell comprising a metallic support 1 ending in a substantially pure electron conducting oxide, an active anode layer 2 consisting of doped ceria, ScYSZ, Ni-Fe alloy, an electrolyte layer 3 consisting of co-doped zirconia based on oxygen ionic conductor, an active cathode layer 5 and a layer of a mixture of LSM and a ferrite as a transition layer 6 to a cathode current collector 7 of single phase LSM. The use of a metallic support instead of a Ni-YSZ anode support increases the mechanical strength of the support and secures redox stability of the support. The porous ferrite stainless steel ends in a pure electron conducting oxide so as to prevent reactivity between the metals in the active anode which tends to dissolve into the ferrite stainless steel causing a detrimental phase shift from ferrite to austenite structure.



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
22 December 2005 (22.12.2005)

PCT

(10) International Publication Number
WO 2005/122300 A3

(51) International Patent Classification:

H01M 8/12 (2006.01) *H01M 4/90* (2006.01)
H01M 4/86 (2006.01) *H01M 8/02* (2006.01)
H01M 4/88 (2006.01)

(21) International Application Number:

PCT/DK2005/000379

(22) International Filing Date: 9 June 2005 (09.06.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

PA 2004 00904 10 June 2004 (10.06.2004) DK
PA 2005 00159 2 February 2005 (02.02.2005) DK

(71) Applicant (for all designated States except US):
FORSKNINGSCENTER RISØ [DK/DK]; Frederiks-
borgevej 399, DK-4000 Roskilde (DK).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **LARSEN, Peter,**
Halvor [DK/DK]; Risø Huse 13, DK-4000 Roskilde
(DK). **MOGENSEN, Mogens, Bjerg** [DK/DK]; Kro-
genlundvej 10, DK-3540 Lynge (DK). **LINDEROTH,**
Søren [DK/DK]; Egevej 47, DK-4000 Roskilde (DK).
HANSEN, Kent, Kammer [DK/DK]; Skelbækvej 86,
DK-3650 Ølstykke (DK). **WANG, Weiguo** [CN/DK];
Havetoften 4 D, DK-2630 Taastrup (DK).

(74) Agent: **GOLDBACH, Klara;** **GRÜNECKER,**
KINKELDEY, STOCKMAIR & SCHWANHÄUSSER,
Maximilianstrasse 58, D-80538 München (DK).

(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, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, 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, 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).

Declaration under Rule 4.17:

— of inventorship (Rule 4.17(iv)) for US only

Published:

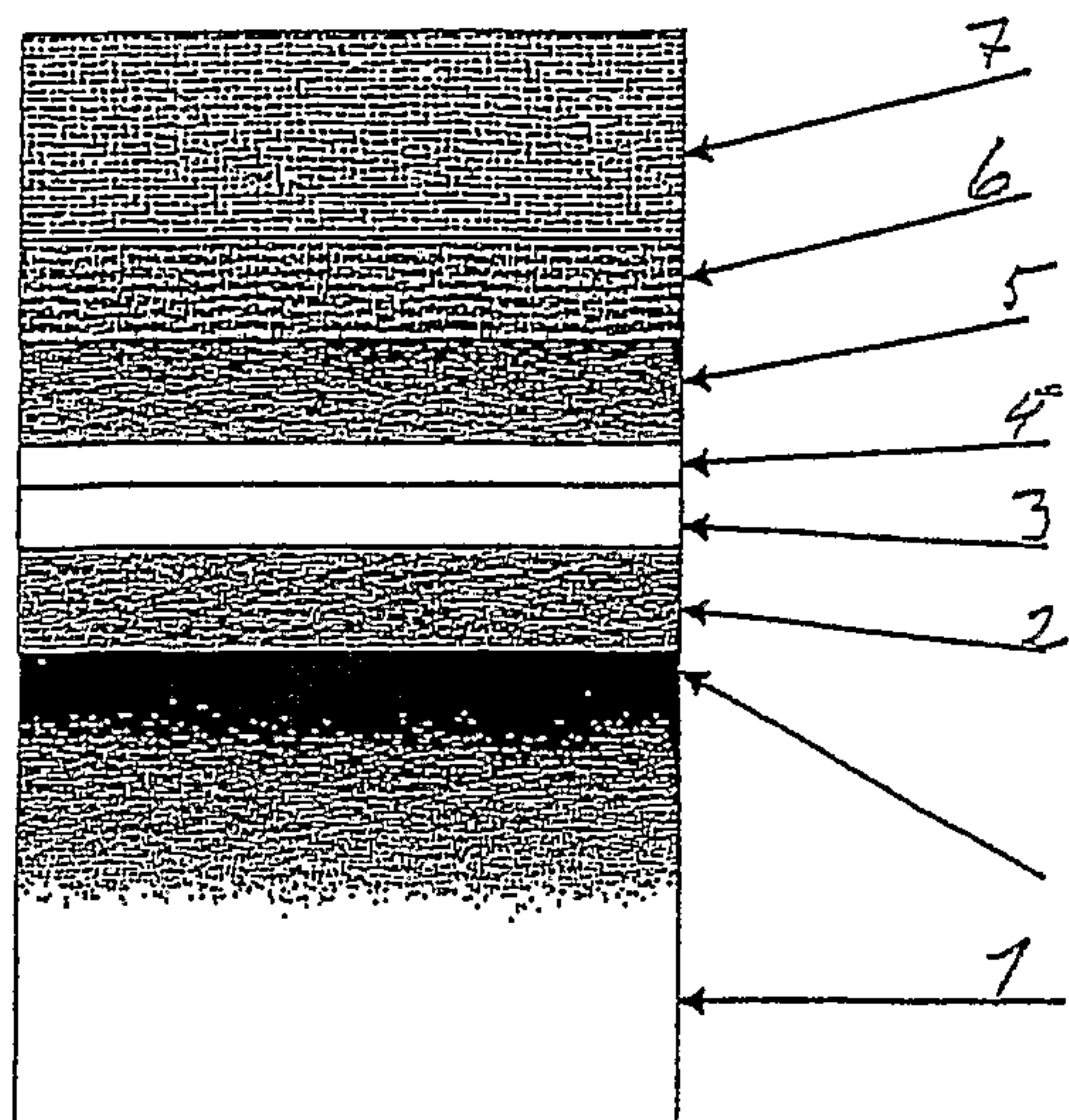
— with international search report
— before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

(88) Date of publication of the international search report:

2 March 2006

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: SOLID OXIDE FUEL CELL



(57) Abstract: SOFC cell comprising a metallic support 1 ending in a sub-
stantially pure electron conducting oxide, an active anode layer 2 consist-
ing of doped ceria, ScYSZ, Ni-Fe alloy, an electrolyte layer 3 consisting of
co-doped zirconia based on oxygen ionic conductor, an active cathode layer
5 and a layer of a mixture of LSM and a ferrite as a transition layer 6 to a
cathode current collector 7 of single phase LSM. The use of a metallic sup-
port instead of a Ni-YSZ anode support increases the mechanical strength
of the support and secures redox stability of the support. The porous fer-
rite stainless steel ends in a pure electron conducting oxide so as to prevent
reactivity between the metals in the active anode which tends to dissolve
into the ferrite stainless steel causing a detrimental phase shift from ferrite
to austenite structure.

WO 2005/122300 A3

Title: Solid oxide fuel cellTechnical Field

- 5 The invention relates to a solid oxide fuel cell (SOFC) comprising a metallic support.

Background Art

US 2002/0048 699 concerns a solid oxide fuel cell comprising a ferritic stainless steel
10 substrate including a porous region and a non-porous region bounding the porous re-
gion. A ferritic stainless steel bipolar plate is located under one surface of the porous
region of the substrate and is sealingly attached to the non-porous region of the sub-
strate above the porous region thereof. A first electrode layer is located over the other
surface of the porous region of the substrate and an electrolyte layer is located over the
15 first electrode layer and a second electrode layer is located over the electrolyte layer.
Such a solid oxide fuel cell is relatively cheap. However it is not sufficiently robust.

Brief Description of the Invention

- 20 The object of the invention is to provide a solid oxide fuel cell which is relatively
cheap and at the same time more robust than previously known.

The SOFC cell according to the invention comprises
a metallic support material,
25 an active anode layer consisting of a good hydrocarbon cracking catalyst,
an electrolyte layer,
an active cathode layer and
a transition layer consisting of preferably a mixture of LSM and a ferritic to the cathode
current collector,
30 means being provided for preventing diffusion between the metallic support and the ac-
tive anode.

The use of a metallic support instead of a Ni-YSZ (Yttria stabilized zirconia) anode support increases the mechanical strength of the support and secures redox stability of the support.

5

A problem when using a metallic support is that during sintering (which takes place at relatively high temperatures) electrode material from the active anode layer interdiffuses with the metallic support, causing for instance a detrimental phase transformation of the support from a ferritic to an austenite phase.

10

According to the invention this may be avoided, either by making the metallic support as a graded cermet structure ending in an electron conducting oxide, or by making the active anode layer as a porous layer into which the active anode material is impregnated after sintering.

15

In a special embodiment according to the invention the cell comprises a ferritic metal support consisting of a graded, layered cermet structure ending in a substantially pure electron conducting oxide,

an active anode layer consisting of a good hydrocarbon catalyst, such as a mixture of

20

doped ceria and Ni-Fe alloy,

an electrolyte layer,

an active cathode layer,

a transition layer consisting preferably of a mixture of LSM ($\text{La}_x\text{Sr}_{1-x}\text{MnO}_3$) and a ferrite and ending in

25

a cathode current collector, preferably consisting of single phase LSM.

The FeCr porous support has on all internal and external surfaces an oxide layer which may be formed either by oxidation in a suitable atmosphere of the Fe-Cr alloy itself or by coating the alloy. The purpose of this coating is to inhibit deposition of carbon and tars. The composition of the coating may be based on e.g. Cr_2O_3 , CeO_2 , LaCrO_3 , SrTiO_3 . In any case the base oxide should be suitably doped.

30

The SOFC cell according to the invention may be provided with a reaction barrier layer of doped ceria between the electrolyte layer and the active cathode said reaction layer having a thickness of 0.1-1 μm . The barrier layer prevents diffusion of cations from the cathode to the electrolyte. As a result the life time may be increased.

According to the invention the active cathode may consist of a composite of one material chosen among scandia and yttria stabilized zirconia (ScYSZ) or doped ceria and one material chosen among, LSM, lanthanide strontium manganate (LnSrMn) or lanthanide strontium iron cobalt oxide (LnSrFeCo), $(\text{Y}_{1-x}\text{Ca}_x)\text{Fe}_{1-y}\text{Co}_y\text{O}_3$, $(\text{Gd}_{1-x}\text{Sr}_x)_s\text{Fe}_{1-y}\text{Co}_y\text{O}_3$ or $(\text{Gd}_{1-x}\text{Ca}_x)_s\text{Fe}_{1-y}\text{Co}_y\text{O}_3$. Such a cathode material performs better than other cathode materials.

According to the invention the electrolyte layer may consist of a co-doped zirconia based oxygen ionic conductor. Such an electrolyte has a higher oxygen ionic conductivity than YSZ and a better long time stability than ScSZ. Doped ceria may be used alternatively.

According to the invention the SOFC cell may comprise a ferritic stainless steel support, an active composite anode layer consisting of a good hydro carbon cracking catalyst, such as Ni-alloys and a suitable ion conductor such as doped ceria or ScYSZ, an electrolyte layer, and active cathode layer and a transition layer consisting preferably of a mixture of LSM and a ferrite to the cathode current collector, preferably consisting of single phase LSM.

25

In a special embodiment the metallic support may consist of a FeCrMx alloy. Mx is an alloying element such as Ni, Ti, Ce, Mn, Mo, W, Co, La, Y, Al. Concentrations are kept below the level of austenite formation, where relevant.

30 In another special embodiment the active anode may consist of a porous layer of 8YSZ, co-doped zirconia or co-doped ceria. 0-50% metal alloy may be added.

Brief Description of the Drawing

The invention will be explained in the following with reference to the drawings in which

5

Fig. 1 illustrates a robust intermediate temperature SOFC cell according to the invention

Fig. 2 illustrates area specific resistances of various cathode materials incl. the cathode material used in the SOFC cell according to the invention.

10

Fig. 3 illustrates a SOFC cell with anode impregnation layer.

Fig. 4 illustrates a SOFC cell with anode impregnation layer and barrier layer.

15

Fig. 5 illustrates a SOFC cell with double electrode impregnation layer.

Best modes for Carrying out the Invention

20 The solid oxide fuel cell SOFC according to the invention is shown in Fig. 1. The cell comprises a metallic support 1 ending in a substantially pure electron conducting oxide, an active anode layer 2 consisting of doped ceria or ScYSZ, Ni-Fe alloy, an electrolyte layer 3 consisting of a co-doped zirconia or ceria based oxygen ionic conductor, an active cathode layer 5 and a layer of a mixture of LSM and a ferrite layer as a transition layer 6 to a cathode current collector 7 of preferably single phase LSM or LnSrMnCo (or a porous metal current collector).

25

The backbone of the complete solid oxide fuel cell which consists of seven functional layers is a functional graded porous metal cermet structure 1 consisting of porous ferritic stainless steel and an electron conducting oxide e.g. $(\text{Sr}_{1-x}\text{La}_x)_s\text{Ti}_{1-y}\text{Nb}_y\text{O}_3$ (LSTN) where $0 \leq x \leq 0.4$, $0.5 \leq s < 1$ and $0 \leq y \leq 1$. Another example of such an oxide is

30

- ($\text{La}_{1-x}\text{Sr}_x$) CrO_3 (LSC). Another example is $\text{Sr}(\text{La})\text{Ti}(\text{Nb})\text{O}_3$ (LSTN)+FSS (e.g. Fe22Cr). In general any electron conducting oxide (n- or p-type conductor) with a thermal expansion coefficient approximately matching the thermal expansion coefficient of the metal may be used. The alloy surface (internal as well as external) is coated with a layer of electron conducting oxide in order to prevent cracking of the hydrocarbon in the porous anode support 1. Cracking of the hydrocarbon should only take place in the active anode as hydrocarbon cracking in the porous support may precipitate carbon leading to plugging of the porosities.
- 10 The use of a metallic support 1 instead of a Ni-YSZ anode support increases the mechanical strength of the support and secures redox stability of the support. The porous ferritic stainless steel 1 ends in pure electron conducting oxide, e.g. LSC or LSTN ($\text{Sr}(\text{La})\text{Ti}(\text{Nb})\text{O}_3$) so as to prevent reactivity between the metals in the active anode 2, especially Ni or NiO, which tends to dissolve into the ferritic stainless steel causing a possible detrimental phase shift from ferritic to austenitic structure. The diffusion may also take place in the opposite direction in that elements from the metal support may diffuse into the anode.
- 15

The active anode layer 2 is a graded structure of doped ceria + ScYSZ + Ni-Fe-alloy, which only contains a few % nano-sized metal catalyst, which is a good hydrocarbon cracking catalyst. The thickness of this layer is 1-50 μm .

20

The active anode 2 is fabricated from solid solutions of NiO and FeO_x or mixtures thereof in ScYSZ and LSTN. This preparation assures a few percent of nano-sized Ni-Fe catalyst after reduction in the operating fuel cell. This allows for a high surface area of the catalyst, and agglomeration of the catalyst is prevented as the catalyst particles are kept at a distance from each other. The small amounts of high surface area nickel and iron allows for fast kinetics of cracking and conversion of the hydrocarbons and for efficient electrochemical conversion of hydrogen. Only by keeping the catalyst finely dispersed the formation of carbon nano-tubes is avoided when hydrocarbons are used as a fuel. The finely dispersed catalyst is formed when the active anode is reduced. As

25

30

the anode only contains a few percent of catalyst it will be redox stable (as only a minor part of the anode will show redox activity). Redox cycling may eventually revive the nanostructure of Ni-Fe catalysts. The anode 2 contains a significant amount of ceria, which has the ability to catalyse the electrochemical oxidation of the carbon, which may be formed as a result of the cracking process.

The electrolyte layer 3 consists of a co-doped zirconia based oxygen ionic conductor (Y,Sc)SZ (Yttria, Scandia Stabilised Zirconia). This type of electrolyte has a higher oxygen ionic conductivity than YSZ and a better long-term stability than ScSZ. Doped ceria may be used alternatively.

The active cathode 5 for a cell with an operation temperature of 550°C may be fabricated from a composite of one material chosen among ScYSZ possibly doped with Ce or doped ceria (e.g. gadolinia doped ceria, CGO), and one material chosen among $(Y_{1-x}Ca_x)Fe_{1-y}Co_yO_3$, $(Gd_{1-x}Sr_x)_sFe_{1-y}Co_yO_3$, $(Gd_{1-x}Ca_x)_sFe_{1-y}Co_yO_3$. The active cathode may also be fabricated from a mixture of doped zirconia or ceria wherein the dopant is Sc, Y, Ce, Ga, Sm, Gd, Ca, any lanthanide element or combinations thereof and $(La, Gd, Sr)(Fe, Co)O_{3-\delta}$. Another example is a graded composite (Y, Ca)FeCoO₃ and doped zirconia or ceria. Such a cathode 5 shows a performance superior to LSM and other cathode materials, cf. Fig. 2. The substitution on the A-site with Y and Ca instead of the commonly used cations La and Sr improves both the performance and the stability of the cathode. The stability is improved as the formation of non-conducting zirconates ($La_2Zr_2O_7$ and $SrZrO_3$) are avoided when using Y and Ca instead of La and Sr. A reaction barrier layer 4 of doped ceria (preventing diffusion of cations from the cathode to the ScYSZ electrolyte) may be necessary to obtain a sufficiently long life time. For fuel cells operating in the temperature range above 700°C an LSM - YSZ or (Y, Sc)SZ composite cathode may be used, and in this case the ceria barrier layer 4 is not needed.

On top of the active cathode layer 5 a graded layer 6 consisting of a mixture of LSM and ferrite or LSM + (Y,Ca)FeCoO₃ is placed as a transition to the cathode current collector 7 of single phase LSM ($La(Sr)MnO_3$) or LSFCo ($La_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$), as this has the highest electron conductivity. The function of the transition layer 6 is to prevent high local thermal stresses due to a small difference in thermal expansion coefficient

between LSM and ferrite. This layer can be avoided when LSM/YSZ is used as a cathode.

Fig. 2 illustrates an Arrhenius plot of various cathodes performances given as area specific resistances (ASR). It appears that GSFCo-ferrite is as good as a cathode containing a noble metal catalyst.

Alternatively an SOFC could be produced with porous electrode impregnation layer(s), so as to omit diffusion between metallic support and the active anode, cf. Fig. 3, layers 11-13.

Layer 11: Metallic support (200-2000 μm), FeCrMx alloys with 0-50 vol% oxide (e.g. doped zirconia, doped ceria or other oxides, such as Al_2O_3 , TiO_2 , MgO , CaO , Cr_2O_3 or combinations thereof, but not limited to such materials). The addition of oxide serves several purposes: 1) enhances the chemical bonding between anode layer and metal support 2) adjusts the thermal expansion coefficient and 3) controls the sinter ability and grain growth.

Layer 12: Porous layer for impregnation of the anode (20-100 μm), Sc-Y-Ga-Ce doped zirconia/Sm-Gd-Y or any Ln element or CaO doped ceria with or without addition of a metal alloy (FeCrMx). In case of addition of a metal support material, the layer will possess oxygen-ion conductivity (doped zirconia/ceria) as well as electronic conductivity (metal). In the case of doped ceria the layer will also have some electro catalytic effect. The anode is completed by impregnation of an electro catalytic component after sintering (Ni with or without doped ceria or any other electro catalyst).

Layer 13: Standard electrolyte ($\sim 10 \mu\text{m}$), similar ionic conducting materials as for layer 12 or LaGaO_3 -based electrolyte.

Layer 14: Full cell; there are two different options as listed below for Figs. 3 and 5.

Fig. 3: Ordinary spraying or screen-printing of cathode.

Fig. 5: Impregnation of second porous layer 14 with cathode.

5 The following advantages are obtained by applying impregnation:

1. Simple, no anode/metal support barrier layer required.
2. Cheap process – only one sintering is required in the case of double impregnation layer.
- 10 3. Sintering is done without the presence of Ni, hence coarsening during sintering is not an issue.
4. Impregnation offers the possibility of obtaining electrodes with high surface areas.
5. Chemical reaction between the electrode material and the other cell materials are
15 prevented/reduced because the operational temperature is lower than the sintering temperature.
6. The composite structure of the impregnation layer ensures a good mechanical bonding between electrolyte and metal support as well as good conductivity across the interfaces.

20

Examples will be given in the following.

Example 1

First step is tape casting of a paste with a composition of Fe-22%Cr ferritic stainless
25 steel with a thickness of 1 mm.

Second step is to tape cast a composite consisting of a 80 wt% $(\text{Sr}_{0.8}\text{La}_{0.2})_{0.95}\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_3$ and 20 wt% Fe-22%Cr paste with a thickness of 5-50 μm on top of the Fe-Cr ferritic steel.

30

Third step is to spray $(\text{Sr}_{0.8}\text{La}_{0.2})_{0.95}\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_3$ in a thickness of 5-50 μm .

Fourth step is to spray the active anode slurry in a thickness of 10 μm . The composition of the slurry is 50 wt% $\text{Y}_{0.04}\text{Sc}_{0.16}\text{Zr}_{0.8}\text{O}_2$ and 50 wt% $\text{Sr}_{0.84}\text{Ni}_{0.05}\text{Fe}_{0.1}\text{TiO}_3$.

5 Fifth step is to spray the electrolyte with a composition of $\text{Y}_{0.04}\text{Sc}_{0.16}\text{Zr}_{0.8}\text{O}_2$ in a thickness of 5 μm .

Sixth step is to co-sinter the resulting half-cell at 1300°C in a reducing atmosphere, 9% H_2 + 91% Ar.

10 Seventh step is to spray the barrier layer consisting of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ in a thickness of 0.2 μm followed by sintering at 700° C.

Eighth step is to coat the Fe-Cr alloy.

15 Ninth step is to spray the cathode consisting of 50 wt% $(\text{Gd}_{0.6}\text{Sr}_{0.4})_{0.99}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ and 50 wt% $\text{Y}_{0.04}\text{Sc}_{0.16}\text{Zr}_{0.8}\text{O}_2$ in a thickness of 20 μm .

Tenth step is to spray 50 wt% $(\text{La}_{0.85}\text{Sr}_{0.15})_{0.95}\text{MnO}_3$ and 50 wt% $(\text{Gd}_{0.8}\text{Sr}_{0.4})_{0.99}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ in a thickness of 1-30 μm .

20

Eleventh step is to screen print the current collector consisting of $(\text{La}_{0.85}\text{Sr}_{0.15})_{0.95}\text{MnO}_3$ with a thickness of 50 μm .

The cathode and the cathode current collector will be in-situ sintered in the stack.

25

The resulting solid oxide fuel cell is robust and is flexible as both hydrocarbons and hydrogen can be converted at the anode. The fuel cell converts hydrocarbons by cracking followed by electrochemical oxidation of the cracking products. As an oxidant either air or pure oxygen could be used.

30

Example 2

First step is tape casting of a paste with a composition of Fe-22%Cr ferritic stainless steel in a thickness of 1 mm.

Second step is to tape cast a composite consisting of a 80 wt% $(\text{Sr}_{0.8}\text{La}_{0.2})_{0.95}\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_3$ and 20 wt% Fe-22%Cr paste with a thickness of 5-50 μm on top of the Fe-Cr ferritic steel.

Third step is to spray $(\text{Sr}_{0.8}\text{La}_{0.2})_{0.95}\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_3$ in a thickness of 5-30 μm .

Fourth step is to spray the active anode slurry in a thickness of 10 μm . The composition of the slurry is 50 wt% $\text{Y}_{0.04}\text{Sc}_{0.16}\text{Zr}_{0.8}\text{O}_{2-\delta}$ and 50 wt% $\text{Sr}_{0.84}\text{Ni}_{0.05}\text{Fe}_{0.1}\text{TiO}_3$

Fifth step is to spray the electrolyte with a composition of $\text{Y}_{0.04}\text{Sc}_{0.16}\text{Zr}_{0.8}\text{O}_{2-\delta}$ in a thickness of 5 μm .

Sixth step is to co-sinter the resulting half-cell at 1300°C in a reducing atmosphere, 9% H_2 + 91% Ar.

Seventh step is to spray the barrier layer consisting of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ in a thickness of 0.2 μm followed by sintering at 700° C.

Eighth step is to coat the Fe-Cr alloy.

Ninth step is to spray the cathode consisting of 50 wt% $(\text{Gd}_{0.6}\text{Sr}_{0.4})_{0.99}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and 50 wt% CGO10 in a thickness of 20 μm .

Tenth step is to spray 50 wt% $(\text{La}_{0.85}\text{Sr}_{0.15})_{0.95}\text{MnO}_3$ and 50 wt% $(\text{Gd}_{0.6}\text{Sr}_{0.4})_{0.99}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ in a thickness of 1-30 μm .

Eleventh step is to screen print the current collector consisting of $(\text{La}_{0.85}\text{Sr}_{0.15})_{0.95}\text{MnO}_3$ with a thickness of 50 μm . The cathode will be in-situ sintered in the stack.

The resulting solid oxide fuel cell is robust and is flexible as both hydrocarbons and hydrogen can be converted at the anode. The fuel cell converts hydrocarbons by cracking followed by electrochemical oxidation of the cracking products. As an oxidant either air or pure oxygen could be used.

Example 3

First step is tape casting of a paste with a composition of Fe-22%Cr ferritic stainless steel with a thickness of 1 mm.

10

Second step is to tape cast a composite consisting of a 80 wt% $(\text{Sr}_{0.8}\text{La}_{0.2})_{0.95}\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_3$ and 20 wt% Fe-22%Cr paste with a thickness of 5-50 μm on top of the Fe-Cr ferritic steel.

15 Third step is to spray $(\text{Sr}_{0.8}\text{La}_{0.2})_{0.95}\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_3$ in a thickness of 1-30 μm .

Fourth step is to spray the active anode slurry in a thickness of 10 μm . The composition of the slurry is 50 wt% $\text{Y}_{0.04}\text{Sc}_{0.16}\text{Zr}_{0.8}\text{O}_{2-\delta}$ and 50 wt% $\text{Sr}_{0.84}\text{Ni}_{0.05}\text{Fe}_{0.1}\text{TiO}_3$.

20 Fifth step is to spray the electrolyte with a composition of $\text{Y}_{0.04}\text{Sc}_{0.16}\text{Zr}_{0.8}\text{O}_{2-\delta}$ in a thickness of 5 μm .

Sixth step is to spray the barrier layer consisting of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ in a thickness of 0.5 μm .

25

Seventh step is to co-sinter the resulting half-cell at 1350°C in a reducing atmosphere, 9% H_2 + 91% Ar.

Eighth step is to coat the Fe-Cr alloy.

30

Ninth step is to spray the cathode consisting of 50 wt% $(\text{Gd}_{0.6}\text{Ca}_{0.4})_{0.99}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ and 50 wt% CGO10 in a thickness of 20 μm .

Tenth step is to spray 50 wt% $(\text{La}_{0.85}\text{Sr}_{0.15})_{0.95}\text{MnO}_3$ and 50 wt% $(\text{Gd}_{0.6}\text{Sr}_{0.4})_{0.99}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ in a thickness of 1-30 μm .

Eleventh step is to screen print the current collector consisting of $(\text{La}_{0.85}\text{Sr}_{0.15})_{0.95}\text{MnO}_3$ with a thickness of 50 μm . The cathode will be in-situ sintered in the stack.

10 The resulting solid oxide fuel cell is robust and is flexible as both hydrocarbons and hydrogen can be converted at the anode. The fuel cell converts hydrocarbons by cracking followed by electrochemical oxidation of the cracking products. As an oxidant either air or pure oxygen could be used.

15 Example 4

First step is tape casting of a paste with a composition of Fe-22%Cr ferritic stainless steel with a thickness of 1 mm.

Second step is to tape cast a composite consisting of a 80 wt% $(\text{Sr}_{0.8}\text{La}_{0.2})_{0.95}\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_3$ and 20 wt% Fe-22%Cr paste with a thickness of 5-50 μm on top of the Fe-Cr ferritic steel.

Third step is to spray $(\text{Sr}_{0.8}\text{La}_{0.2})_{0.95}\text{Ti}_{0.9}\text{Nb}_{0.1}\text{O}_3$ in a thickness of 1-30 μm .

25 Fourth step is to spray the active anode slurry in a thickness of 10 μm . The composition of the slurry is 50 wt% $\text{Y}_{0.04}\text{Sc}_{0.16}\text{Zr}_{0.8}\text{O}_{2-\delta}$ and 50 wt% $\text{Sr}_{0.84}\text{Ni}_{0.05}\text{Fe}_{0.1}\text{TiO}_3$.

Fifth step is to spray the electrolyte with a composition of $\text{Y}_{0.04}\text{Sc}_{0.16}\text{Zr}_{0.8}\text{O}_{2-\delta}$ in a thickness of 5 μm .

Sixth step is to co-sinter the resulting half-cell at 1350° C in a reducing atmosphere, 9% H₂+ 91% Ar.

Seventh step is to spray the cathode consisting of 50 wt% LSM and 50 wt%
 5 Y_{0.04}Sc_{0.16}Zr_{0.8}O_{2-δ} in a thickness of 20 μm.

Eighth step is to screen print the current collector consisting of (La_{0.85}Sr_{0.15})_{0.95}MnO₃ with a thickness of 50 μm. The cathode will be in-situ sintered in the stack.

10 The resulting solid oxide fuel cell is robust and is flexible as both hydrocarbons and hydrogen can be converted at the anode. The fuel cell converts hydrocarbons by cracking followed by electrochemical oxidation of the cracking products. As an oxidant either air or pure oxygen could be used.

15 Example 5

First step is tape casting of a paste with a composition of Fe-22%Cr ferritic stainless steel with a thickness of 1 mm.

Second step is to tape cast a composite consisting of a 80 wt% (Sr_{0.8}La_{0.2})_{0.95}Ti_{0.9}
 20 Nb_{0.1}O₃ and 20 wt% Fe-22%Cr paste with a thickness of 5-50 μm top of the Fe-Cr ferritic steel.

Third step is to spray (Sr_{0.8}La_{0.2})_{0.95}Ti_{0.9}Nb_{0.1}O₃ in a thickness of 1-30 μm.

25 Fourth step is to spray the active anode slurry in a thickness of 10 μm. The composition of the slurry is 50 wt% Y_{0.04}Sc_{0.16}Zr_{0.8}O_{2-δ} and 50 wt% Sr_{0.84}Ni_{0.05}Fe_{0.1}TiO₃.

Fifth step is to spray the electrolyte with a composition of Y_{0.04}Sc_{0.16}Zr_{0.8}O_{2-δ} in a thickness of 5 μm.

Sixth step is to co-sinter the resulting half-cell at 1350°C in a reducing atmosphere, 9% H₂ + 91% Ar.

Seventh step is to spray the cathode consisting of 50 wt% LSM and 50 wt% Y_{0.04} Sc_{0.16} Zr_{0.8}O_{2-δ} in a thickness of 20 μm.

Eighth step is to screen print the current collector consisting of (La_{0.85}Sr_{0.15})_{0.95}MnO₃ with a thickness of 50 μm.

10 The cathode will be in-situ sintered in the stack.

The resulting solid oxide fuel cell is robust and is flexible as both hydrocarbons and hydrogen can be converted at the anode. The fuel cell converts hydrocarbons by cracking followed by electrochemical oxidation of the cracking products. As an oxidant either air or pure oxygen could be used.

Example 6

Support sheets with a thickness in the range of 200-2000 μm are manufactured by tape-casting a Fe22Cr alloy (+ minor constituents such as Mn) powder suspension, cf. Fig. 3. After drying of the support 11 a layer for anode impregnation (layer 12, 50 μm) and finally a electrolyte layer (layer 13, 10 μm) are deposited by spray painting. Both layers have a composition of Zr_{0.78}Sc_{0.20}Y_{0.02}O_{2-δ}. The suspensions for spraying are made so that the impregnation layer 12 has at least 40% porosity with an average pore size of 1-3 μm and the electrolyte is dense after sintering. Samples are subsequently punched out in the desired dimensions, and the so-called half-cells are sintered under controlled reducing conditions. A solution of Ni-, Ce-, Gd-nitrates is impregnated into the porous zirconia layer 12 by vacuum infiltration. The resulting anode will have volume concentration of 40% Ni and 60% (Gd_{0.1}Ce_{0.9})O_{2-δ}. After drying and cleaning of the electrolyte surface a (Gd_{0.6}Sr_{0.4})_{0.99}(Co_{0.2}Fe_{0.8})O_{3-δ} cathode (layer 14, 40 μm) is deposited by spray painting.

Example 7

Support sheets with a thickness in the range of 200-2000 μm are manufactured by tape-casting a Fe22Cr alloy (with minor additional constituents) powder suspension, cf. Fig. 3. After drying of the support (11) a layer for anode impregnation (layer 12, 50 μm) is deposited by screen-printing an ink comprising a 1:1 volume mixture of $\text{Zr}_{0.78}\text{Sc}_{0.20}\text{Y}_{0.02}\text{O}_{2-\delta}$ and FeCr alloy. The addition of metal to the impregnation layer ensures a good bonding between the metal support and the impregnation layer. Finally an electrolyte layer (layer 13, 10-15 μm) is deposited by spray painting. The cell is completed as described in example 6.

Example 8

Support sheets with a thickness in the range of 200-2000 μm are manufactured by tape-casting a Fe22Cr alloy (with minor constituents) powder suspension mixed with 2-10 vol% $\text{Zr}_{0.94}\text{Y}_{0.06}\text{O}_{2-\delta}$, cf. Fig. 3. The cell is completed as described in example 7.

Example 9

Support sheets with a thickness in the range of 200-2000 μm are manufactured by tape-casting a Fe22Cr alloy (with minor constituents) powder suspension, cf. Fig. 3. A graded impregnation layer is made from one or more of thin sheets comprising a mixture of electrolyte material and metal alloy (FeCrM_x). Sheets with varying grain sizes and resulting pore sizes and with thicknesses of 30-70 μm are manufactured by tape-casting powder suspensions. The cell structure is made by laminating metal support sheet and 1-4 impregnation layers sheets by rolling or pressing. The resulting impregnation layer is graded in composition with pore size and grain size ranging from 5-10 μm against the metal support down to ~ 1 μm at the electrolyte interface. The cell is completed as described in Example 6.

Example 10

As example 9, but with the addition of pore formers to control the final porosity of the impregnation layer and metal support.

Example 11

As example 10, but with the addition of sintering additive (15) to control the shrinkage of the layers. Examples of which include, but are not limited to Al_2O_3 , MgO , CaO ,
5 SrO , CoO_x , MnO_x , B_2O_3 , CuO_x , ZnO_2 , VO_x , Cr_2O_3 , FeO_x , NiO , MoO_x , WO_3 , Ga_2O_3 or in combinations thereof.

Example 12

A half-cell as described in previous examples is manufactured. A cathode/electrolyte
10 barrier layer 14, (Fig. 4), ($0.5\ \mu\text{m}$) is deposited on the electrolyte surface by spin coating of a Gd-Ce nitrate solution. After sintering of the barrier layer at $700\ ^\circ\text{C}$ a Ni-
($\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$) anode is impregnated into layer 12, as described in example 6. After drying and cleaning of the electrolyte surface a ($\text{La}_{0.6}\text{Sr}_{0.4}\text{O}_{0.99}$) ($\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$) cathode
(layer 5, $40\ \mu\text{m}$) is deposited by screen printing.

15

Example 13

Support sheets with a thickness of approximately $800\ \mu\text{m}$ are manufactured by rolling a Fe22 Cr alloy paste, layer 11 in Fig. 3. After drying of the support, a layer for anode
impregnation (layer 12) and an electrolyte layer are deposited by screen-printing. Both
20 layers have a composition of ($\text{Sm}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$). Inks for screen-printing are made so that the impregnation layer has $>50\%$ porosity with an average pore size of $1\text{-}2\ \mu\text{m}$ and the electrolyte is dense. Samples are subsequently punched out in the desired dimensions and the so-called half-cells are sintered under controlled reducing conditions.

25 A solution of Ni nitrate is prepared and impregnated into the porous ($\text{Sm}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$) layer (layer 12) by immersion. After drying and cleaning of the electrolyte surface, a
($\text{La}_{0.6}\text{Sr}_{0.4}\text{O}_{0.99}$) ($\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$) cathode (layer 14) is deposited by spray painting.

30 Example 14

Support sheets with a thickness of approximately 500 μm are manufactured by tape-casting a Fe22Cr alloy powder suspension containing 5 vol% $(\text{Gd}_{0.1}\text{Ce}_{0.9})\text{O}_{2-\delta}$ to enhance the bonding to the impregnation layer, cf. Fig. 3. A layer for anode impregnation (30 μm) and finally an electrolyte layer (10 μm) are deposited by spray painting. Both
 5 layers have a composition of $(\text{Gd}_{0.1}\text{Ce}_{0.9})\text{O}_{2-\delta}$. After sintering, a nitrate solution of Ni, Gd and Ce is impregnated into the porous ceria layer by vacuum infiltration. After drying and cleaning of the electrolyte surface, a LSCF cathode is deposited by screen printing.

10 Example 15

A support is manufactured as explained in Example 8. A layer for anode impregnation (30 μm) comprising Fe-Cr alloy powder and $(\text{Gd}_{0.1}\text{Ce}_{0.9})\text{O}_{2-\delta}$ in a 1:1 volume ratio and a $(\text{Gd}_{0.1}\text{Ce}_{0.9})\text{O}_{2-\delta}$ electrolyte layer (10 μm) are deposited by spray painting. The cell is completed as explained in Example 6.

15

Example 16

A support is manufactured as explained in Example 6, (layer 11 in Fig. 3). After drying of the support, a layer for electrode impregnation, (layer 12, 70 μm), a $\text{Zr}_{0.78}\text{Sc}_{0.20}\text{Y}_{0.02}\text{O}_{2-\delta}$ electrolyte layer, (layer 13, 10 μm), and finally another layer for
 20 electrode impregnation, (layer 14, 30 μm), are deposited by spray painting. Both impregnation layers have a composition of $\text{Zr}_{0.78}\text{Sc}_{0.20}\text{Y}_{0.02}\text{O}_{2-\delta}$ with 40 vol% FeCr powder with an approximate porosity of ~60% porosity.

Samples are subsequently punched out in the desired dimensions, and the samples are
 25 sintered under controlled reducing conditions. Layer 14 is masked and a solution of Ni-Ce-, Gd-nitrates is impregnated into the porous layer 12 by vacuum infiltration. The resulting anode will have a volume concentration of 40% Ni and 60% $(\text{Gd}_{0.1}\text{Ce}_{0.9})\text{O}_{2-\delta}$. After drying the mask on layer 14 is removed, layer 12 is masked and the active cathode material is impregnated by vacuum infiltration in a nitrate solution (resulting cathode composition): $(\text{Gd}_{0.6}\text{Sr}_{0.4})_{0.99}(\text{Co}_{0.2}\text{Fe}_{0.8})\text{O}_{3-\delta}$.
 30

Example 17

A cell structure is manufactured as described in example 6. The anode layer is made by pressure impregnation of a nano-sized suspension of NiO and $(\text{Gd}_{0.1}\text{Ce}_{0.9})\text{O}_{2-\delta}$.

5 Example 18

As example 7, but characterised by the use of sintering additives (one or more chosen from, but not limited to, the list given in example 12) that allows suitable sintering of the respective components under oxidising conditions at temperatures below 1100° C.

CLAIMS:

1. A solid oxide fuel cell comprising
a metallic support material,
an active anode layer consisting of a hydrocarbon cracking catalyst,
an electrolyte layer,
a reaction barrier layer of doped ceria between the electrolyte layer and the active cathode layer,
an active cathode layer, and
a transition layer to a cathode current collector with means being provided for preventing diffusion between the metallic support and the active anode.
2. The solid oxide fuel cell according to claim 1, characterized by the diffusion between the metallic support and the active anode has been prevented by the metallic support being graded, ending in a substantially pure electron conducting oxide.
3. The solid oxide fuel cell according to claim 2, characterized by the metallic support being composed of a FeCrM_x alloy, with M_x being Ni, Ti, Ce, Mn, Mo, W, Co, La, Y or Al.
4. The solid oxide fuel cell according to any one of claims 1 or 2, characterized by the active anode layer consisting of a hydrocarbon cracking catalyst being a mixture of doped ceria and a Ni-Fe alloy.
5. The solid oxide fuel cell according to any one of claims 1 to 4, characterized by the transition layer consisting of a mixture of lanthanum strontium manganite and a ferrite, and ending in a cathode current collector consisting of single phase lanthanum strontium manganite.
6. The solid oxide fuel cell according to claim 1, characterized by the reaction barrier having a thickness of 0.1 to 1 μm .

7. The solid oxide fuel cell according to any one of claims 1 to 6, characterized by the active cathode consisting of a composite of one material which is ScYSZ or doped ceria, and one material which is lanthanum strontium manganite, LnSrMn , $\text{LnSrFeCo} (\text{Y}_{1-x}\text{Ca}_x)\text{Fe}_{1-y}\text{Co}_y\text{Co}_3$, $(\text{Gd}_{1-x}\text{Sr}_x)\text{Fe}_{1-y}\text{Co}_y\text{O}_3$ or $(\text{Gd}_{1-x}\text{Ca}_x)_s\text{Fe}_{1-y}\text{Co}_y\text{O}_3$.
8. The solid oxide fuel cell according to any one of claims 1 to 6, characterized by the electrolyte layer consisting of a co-doped zirconia or a co-doped ceria based oxygen ionic conductor.
9. The solid oxide fuel cell according to claim 8, characterized by the electrolyte layer having a thickness of about 0.1 to 20 μm .
10. The solid oxide fuel cell according to claim 1, characterized by the active anode having a thickness of 1 to 50 μm .
11. The solid oxide fuel cell according to claim 1, characterized by the transition layer being composed of single phase lanthanum strontium manganite.
12. The solid oxide fuel cell according to claim 3, characterized by a coating of the internal and external surfaces of the Fe-Cr M_x metal support, wherein the Fe-Cr M_x metal support is a porous support.
13. The solid oxide fuel cell according to claim 1, characterized by the metallic support being made of a Fe-Cr containing alloy with an addition of up to 50% metal oxides.
14. A solid oxide fuel cell comprising
 - a metallic support material,
 - an active anode layer comprising a hydrocarbon cracking catalyst, characterized by the anode layer comprising doped zirconia or doped ceria wherein the dopant is Sc, Y, Ce, Ga, Sm, Gd, Ca, any lanthanide element, or a combination thereof,
 - an electrolyte layer,
 - an active cathode layer, and

a transition layer to a cathode current collector with means being provided for preventing diffusion between the metallic support and the active anode, wherein the diffusion between the metallic support and the active anode being prevented by the anode layer consisting of a porous material, said porous material being impregnated after sintering.

15. The solid oxide fuel cell according to claim 13, characterized by said metal oxides added to the support material being doped is zirconia, doped ceria, Al_2O_3 , TiO_2 , MgO , CaO , Cr_2O_3 , FeO_x , or a combination thereof.
16. The solid oxide fuel cell according to claim 14, characterized by the anode layer further comprising a metal alloy.
17. The solid oxide fuel cell according to any one of claims 14 to 16, characterized by the electrolyte consisting of doped zirconia or doped ceria wherein the dopant is Sc, Y, Ce, Ga, Sm, Gd, Ca or a combination thereof.
18. The solid oxide fuel cell according to any one of claims 14 to 17, characterized by the active anode consisting of a porous layer of doped zirconia or doped ceria wherein the dopant is Sc, Y, Ce, Ga, Sm, Gd, Ca, any lanthanide element or a combination thereof, with a metallic catalyst.
19. The solid oxide fuel cell according to any one claims 1 to 18, characterized by the active cathode consisting of a mixture of doped zirconia or ceria wherein the dopant is Sc, Y, Ce, Ga, Sm, Gd, Ca, any lanthanide element, or a combination thereof, and $(\text{La}, \text{Gd}, \text{Sr})(\text{Fe}, \text{Co})\text{O}_{3-\delta}$.
20. The solid oxide fuel cell according to any one of claims 14 to 19, characterized by a second active electrode layer consisting of a porous layer, into which the active cathode is impregnated after sintering.

21. The solid oxide fuel cell according to claim 20, characterized by the cathode layer consisting of doped zirconia or doped ceria wherein the dopant is Sr, Y, Ce, Ga, Sm, Gd, Ca, any lanthanide element, or a combination thereof.
22. The solid oxide fuel cell according to claim 21, characterized by the cathode layer consisting of doped zirconia or doped ceria wherein the dopant is Sr, Y, Ce, Ga, Sm, Gd, Ca, any lanthanide element, or a combination thereof, mixed with metal alloy.
23. The solid oxide fuel cell according to claim 20, characterized by the electrolyte consisting of doped zirconia or doped ceria wherein the dopant is Sc, Y, Ce, Ga, Sm, Gd, Ca or a combination thereof.
24. The solid oxide fuel cell according to claim 20, characterized by the active anode consisting of a porous layer of doped zirconia or doped ceria wherein the dopant is Sc, Y, Ce, Ga, Sm, Gd, Ca, any lanthanide element or a combination thereof, with a metallic catalyst.
25. The solid oxide fuel cell according to claim 20, characterized by the active cathode consisting of mixture of doped zirconia or doped ceria wherein the dopant is Sc, Y, Ce, Ga, Sm, Gd, Ca, any lanthanide element, or a combination thereof, and $(\text{LaGdSr})(\text{FeCo})\text{O}_{3-\delta}$.

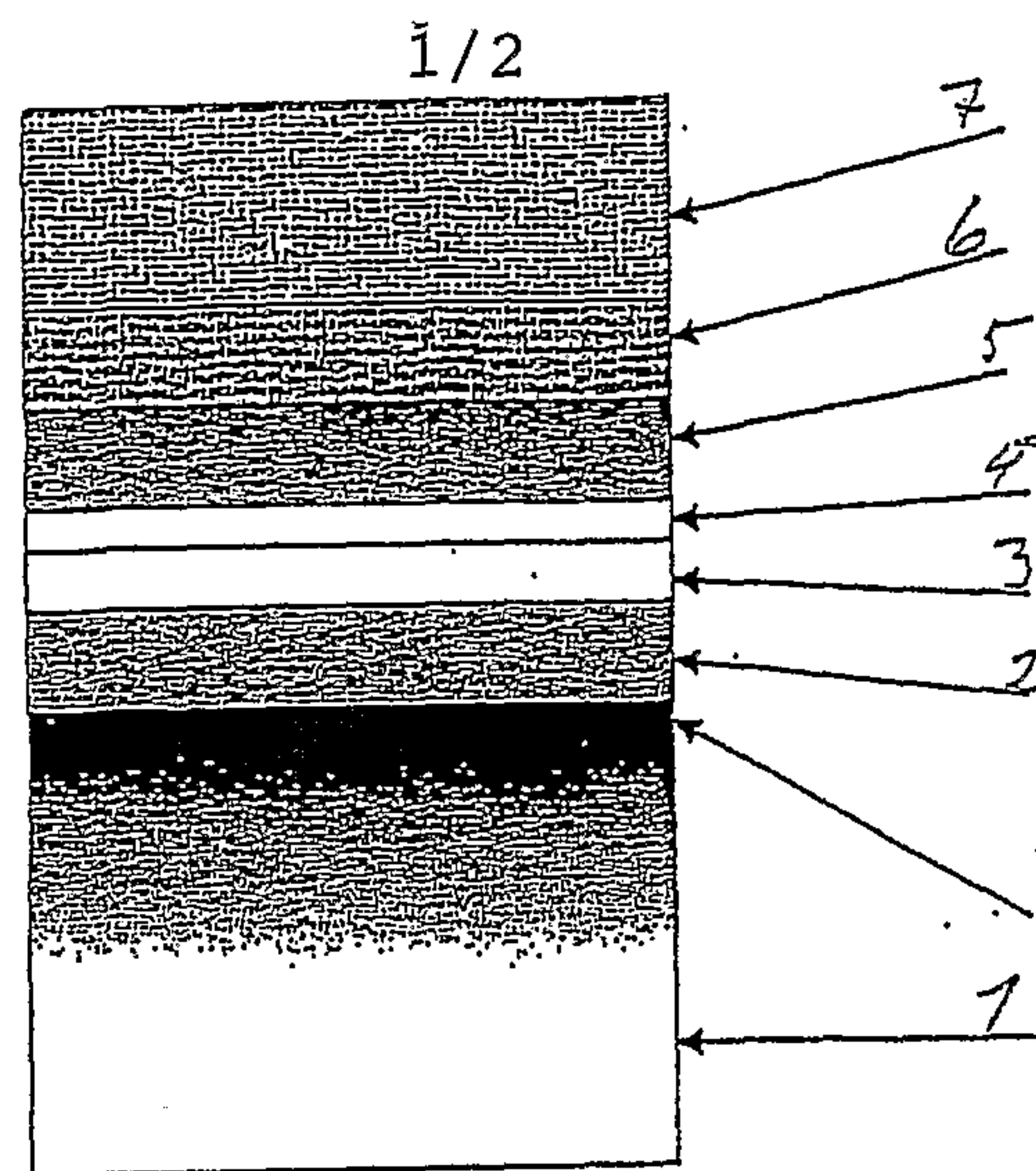


Fig. 1

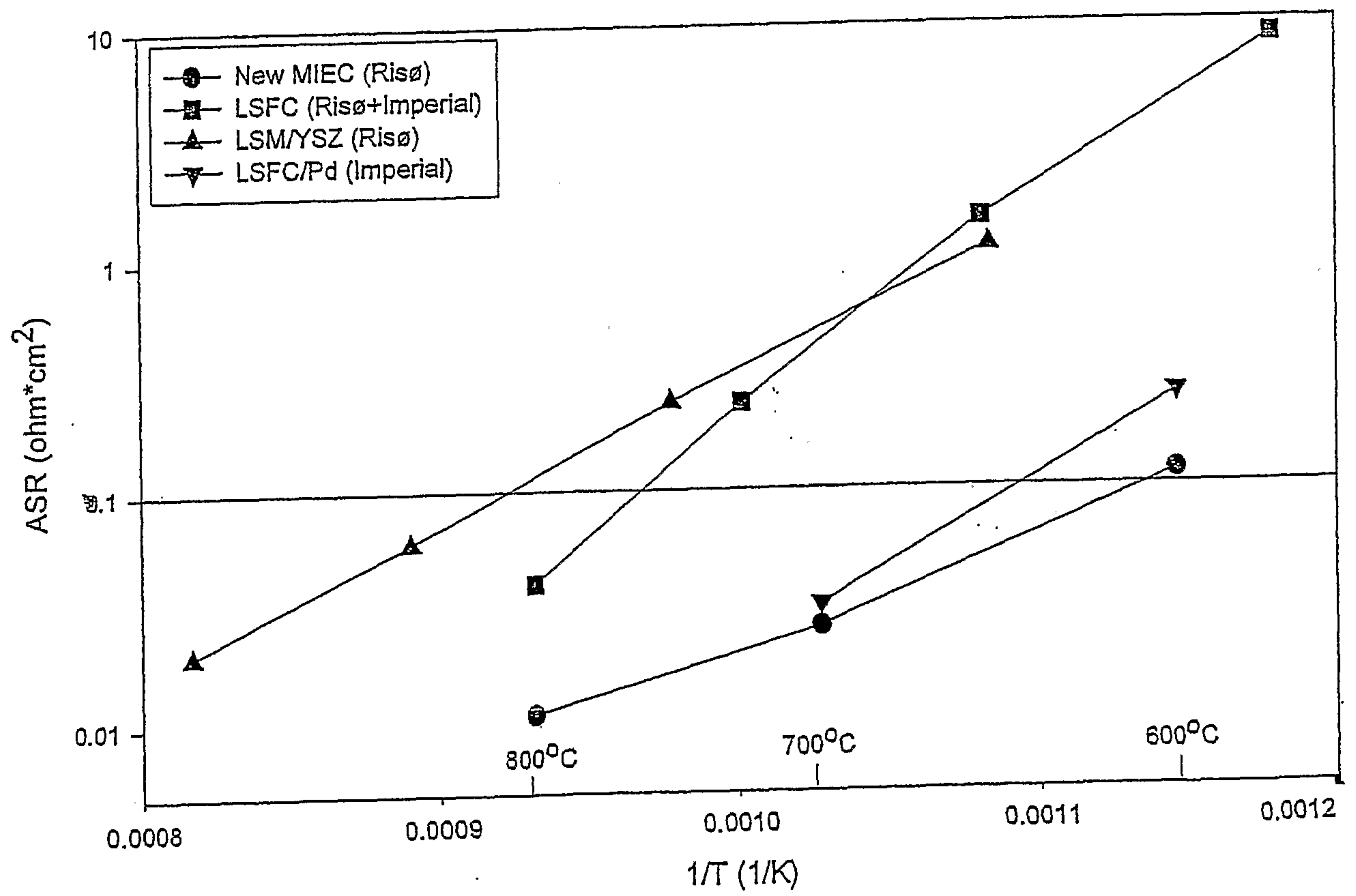


Fig. 2

2/2

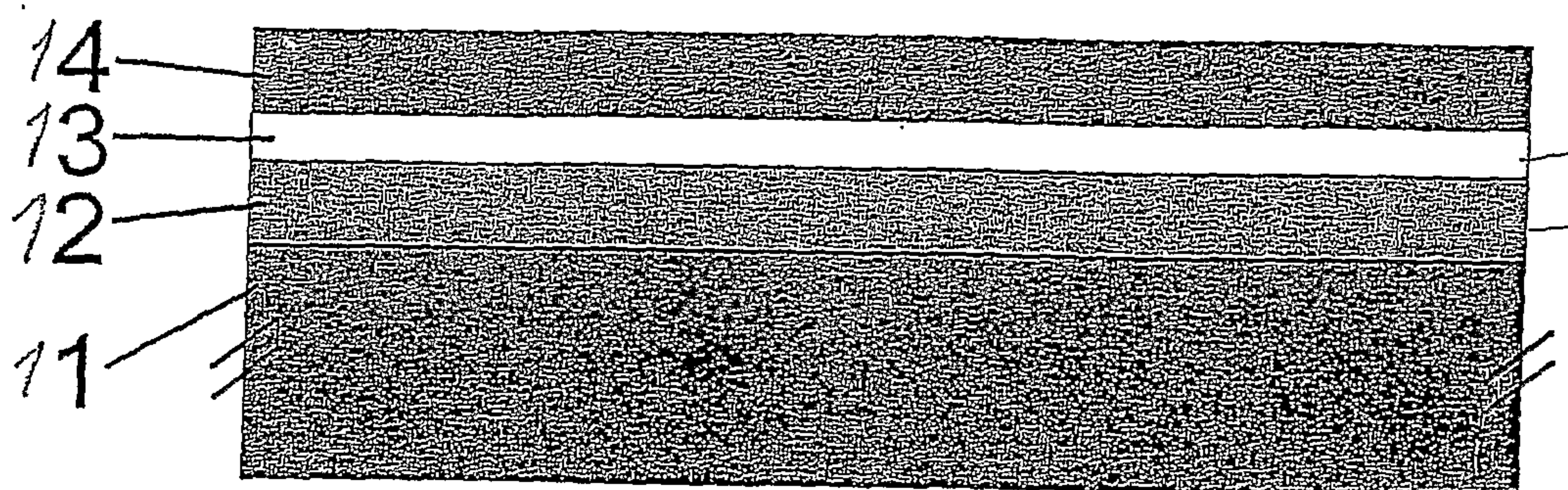


Fig. 3

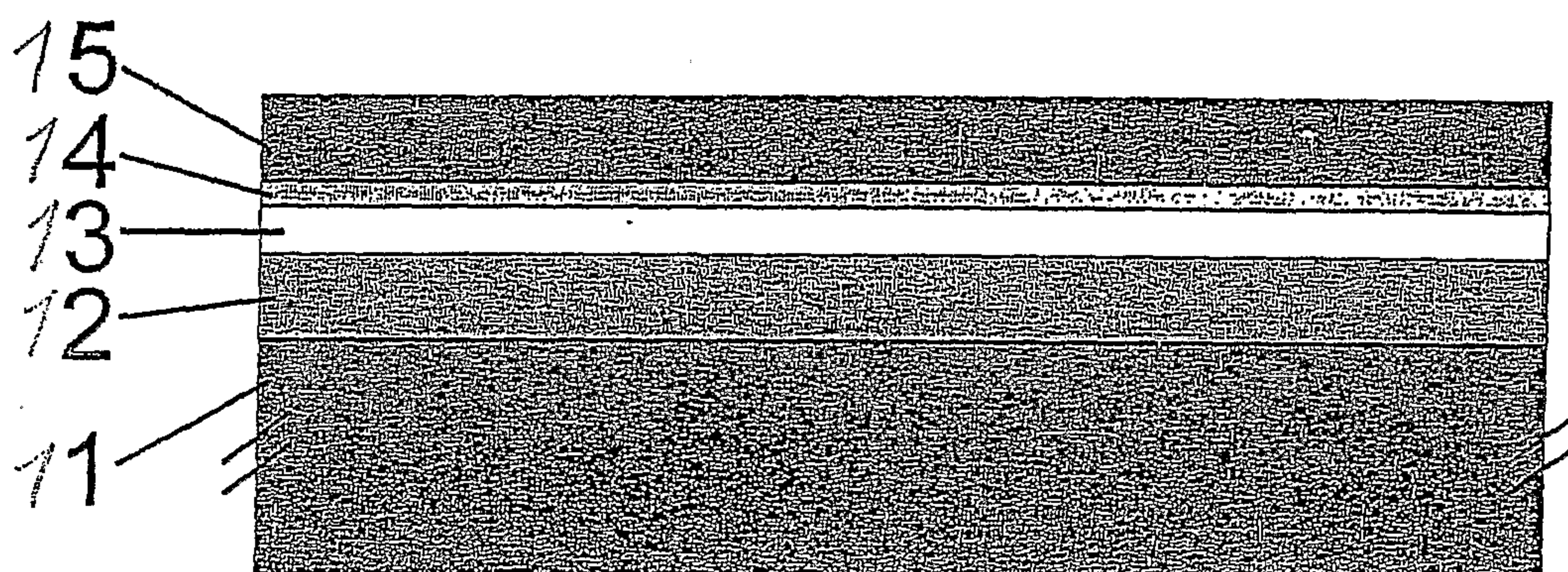


Fig. 4

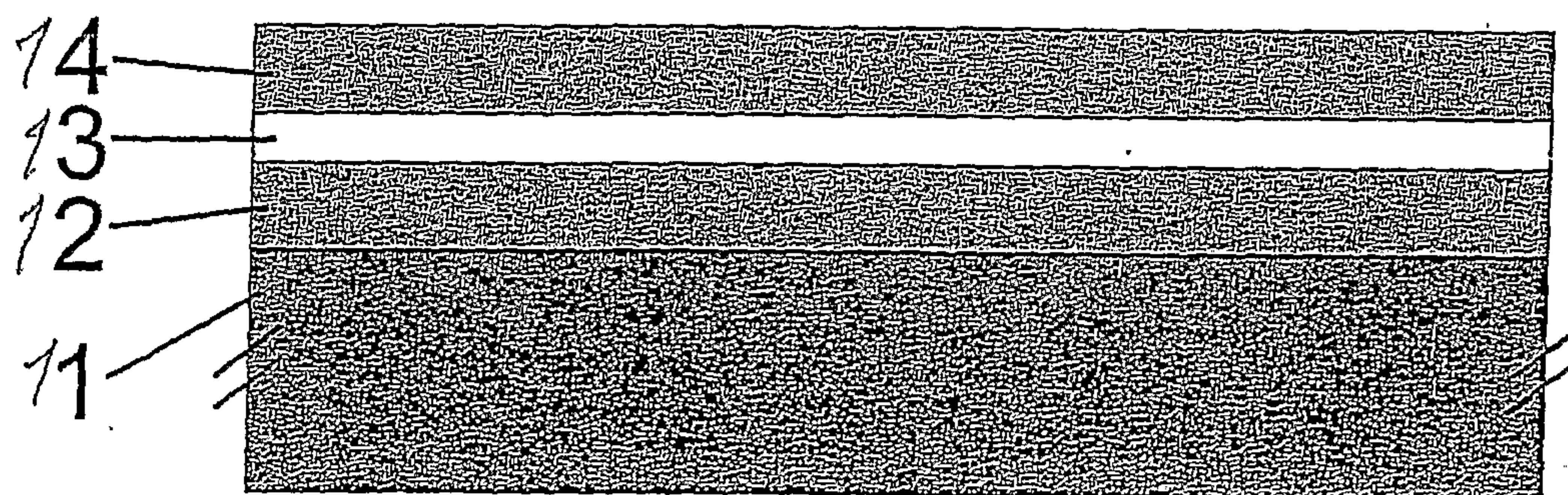


Fig. 5

