

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

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
3 September 2009 (03.09.2009)

PCT

(10) International Publication Number
WO 2009/106933 A1

(51) International Patent Classification:

H01M 4/90 (2006.01) *H01M 4/86* (2006.01)
H01M 8/12 (2006.01) *H01M 8/06* (2006.01)
H01M 8/14 (2006.01)

(21) International Application Number:

PCT/IB2008/050729

(22) International Filing Date:

28 February 2008 (28.02.2008)

(25) Filing Language:

English

(26) Publication Language:

English

(71) Applicant (for all designated States except US): **ECOLE POLYTECHNIQUE FEDERALE DE LAUSANNE (EPFL)** [CH/CH]; Sri-cm2, Station 10, CH-1015 Lausanne (CH).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **THAMPI, K. Ravindranathan** [IN/CH]; Chemin de Curtenaux 23 B, CH-1023 Crissier (CH). **MCEVOY, Augustin J.** [CH/CH]; Ch. Près-les-Bois 64, CH-1066 Epalinges (CH). **EL ROUSTOM, Bahaa** [LB/CH]; Rue du Simplon 4, CH-1006 Lausanne (CH).

(74) Agents: **GANGUILLET, Cyril** et al.; ABREMA Agence Brevets et Marques, Ganguillet, Avenue du Théâtre 16, CP 5027, CH-1002 Lausanne (CH).

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

— with international search report (Art. 21(3))

(54) Title: DESENSITISED FUEL CELL SYSTEM

(57) Abstract: The present invention relates to a system using and/or processing fuel, wherein a catalytically active element is desensitised to impurities present in the fuel. The inventors thus surprisingly found that a fuel processing system, which may be a fuel cell or a sub-unit of a fuel cell system, could be successfully protected from impurities, in particular elemental sulfur and compounds containing sulfur. The protective effect is obtained by using an additive, preferably a halogen, in the preparation of the catalytically active element.



WO 2009/106933 A1

Desensitised Fuel Cell System

Technical Field

5 The present invention relates to the field of fuel processing systems, in particular fuel processing systems where any kind of fuel is subjected to a catalyzed reaction. The present invention thus relates to a system using and/or processing a fuel, to a method of desensitising an element in a fuel processing system against impurities present in fuel and in particular to the use of halides or halide compounds for desensitising elements of fuel cell systems.

10

Prior Art and the Problem Underlying the Invention

Fuel Cells directly convert chemical energy to electrical energy, without any Carnot limitations. Hence their energy efficiencies are relatively high. Among the various types of
15 fuel cells, Solid Oxide Fuel Cells (SOFC) and Molten Carbonate Fuel Cells (MCFC) are operated at high temperatures and in principle, can run on various fuels such as natural gas (primarily methane), LPG, naphtha and hydrogen. Like any other electrochemical cell, a fuel cell has an electrolyte, a cathode (air side) and an anode (fuel side). SOFCs use a solid ion conducting electrolyte (for example, yttria stabilised zirconia, YSZ). The fuel is oxidised on
20 the anode side and to effect the oxidation process, the electrolyte transports the required O^{2-} from the cathode side. SOFCs are able to generate both electricity and high quality heat, which may be used for space heating or combined cycle applications. The most preferred fuel for commercial or industrial SOFC operation is natural gas.

25 At this time, practically all SOFC anodes use a nickel-zirconia cermet composite. While there has been significant development in these anodes, particularly in control of materials quality and structural morphology, this system in fact dates from the late 1960's (H.S. Spacil, US 3,503,809). The dominance of this cermet concept confirms its validity even today. In principle, the ability of SOFC to electrochemically oxidize hydrocarbons, alcohols, or even
30 biogas eliminates the need for an external fuel processor, thus reducing the overall cost and complexity.

However, in practice, while very effective as an oxidation site for hydrogen, and to almost the same extent for carbon monoxide, the cermet anode still presents obvious weaknesses, which

must be taken into account in cell and stack design as well as by observation of operating restrictions. In particular, direct feeding of commercial hydrocarbon fuels to the anode of conventional solid oxide fuel cells creates problems associated with the anode deactivation by carbon deposition (coking). This problem is avoided by conducting an external reforming of the hydrocarbon fuel by the aid of a catalyst, in which the hydrocarbon, for example, CH₄, is converted to CO and H₂. Reforming pre-processing steps increase the overall size and complexity of fuel cell systems and efforts have been undertaken to improve anode properties by finding ways of reducing anode degradation due to hydrocarbons. In US 2004/0166394, novel anode materials are disclosed, having low surface degradation when fed directly with hydrocarbons.

Besides reforming sub-systems, the complexity of state of the art fuel cell systems is increased by other pre-processing systems, in particular pre-processing systems designed to remove impurities present in the fuel. Commercial natural gas and other hydrocarbon fuels contain traces of components present as impurities or even additives (for example as odorants due to safety regulations) that act as catalyst poisons deactivating the anode and dramatically affecting the performance of the fuel cell. Sulfur (S) is the most prominent contaminant in this context. Ni-cermets are in practice particularly susceptible to deactivation and corrosion due to S impurities in the fuel. During the above mentioned reforming process S is converted to gaseous hydrogen sulfide (H₂S). An essential component in any large-scale SOFC system is therefore a desulfuriser unit, which adds to capital and maintenance costs.

An informative publication on the damage caused by Sulfur impurities was provided by M. Smith and A. J. McEvoy, "Regeneration of Anodes Exposed to Sulfur", Electrochemical Society Transactions, 7(1) 373, 2007.

Sulfur not only suppresses the electrocatalytic properties of the Ni in the cermet, but also affects its thermal and redox stability. Since the state of the art cermet anode is the result of four decades of research and development, it is preferable to build on that and focus on the minimum modifications necessary to secure carbon resistance, redox stability and desensitisation to sulfur. Very recently it has been reported that nickel cermets can be desensitised to sulfur by introduction of hydrodesulfurisation (HDS) catalysts (M. Smith and A. J. McEvoy, 2007). It is based on heavy transition metals derived from petrochemicals industry experience (J.G. Kushmerick, S.A. Kandel, P. Han, J.A. Johnson and P.S. Weiss, J.

Phys. Chem. B, 104, 2980, 2000). This solution is more obvious and direct, when compared to the formulation of a novel material tolerant to sulfur, which also satisfies all the operational requirements of SOFC.

- 5 The above said illustrates cost and reliability as important barriers to widespread SOFC implementation. It is therefore an objective underlying the present invention to contribute to the reduction of the overall complexity of fuel cell systems and to the removal of existing barriers to widespread SOFC implementation.
- 10 Particularly, it is an objective of the present invention to reduce the sensitivity of fuel processing systems to impurities or additives present in fuels, such as commercial natural gas. It is an objective to reduce the sensitivity of catalytic elements in fuel processing systems, in particular fuel cell systems.
- 15 More particularly, it is an objective of the present invention to reduce the sensitivity of fuel processing systems, in particular fuel cells, to impurities containing sulfur in the fuel. For example, it is an objective to provide a fuel cell that does not suffer loss of performance due to impurities containing sulfur in the fuel.
- 20 It is an objective of the present invention to provide means for protecting catalytically active elements of one but preferably several or all subsystems of a fuel processing system from impurities present in the fuel. For example, it is an objective to protect a reforming subsystem as well as a fuel cell as such from impurities, and other possibly present subsystems of a larger fuel processing system.
- 25 Furthermore, it is an objective of the present invention to provide a catalytically active element, for example an anode of a fuel cell system, wherein said catalytically active element is desensitised to sulfur and sulfur compounds, such as H₂S, thiophene, ammonium sulfide, for example.

30

Summary of Invention

The inventors of the present invention provide a system using and/or processing a fuel, the system comprising one or more elements having a catalytic activity, wherein degradation

and/or deactivation of said catalytic activity due to impurities present in the fuel is substantially reduced. The catalytically active element preferably comprises an additive assisting in the desensitisation of the element to the impurities, so that loss of catalytic activity due to the impurities is to a large extent reduced.

5

In a first aspect, the present invention provides a system using and/or processing a fuel, the system comprising one or more elements having a catalytic activity, wherein the element comprises at least one stabilising additive capable of protecting the catalytic activity of said element in presence of said impurity.

10

In a second aspect, the present invention provides a method of desensitising an element of a system using and/or processing a fuel against impurities potentially present in the fuel, wherein the fuel is suitable to be consumed by the system, the method comprising the step of incorporating at least one protective additive in and/or on said element. The protective additive may be incorporated on the surface and/or in the bulk of the element.

15

In a third aspect, the present invention provides a method of protecting a catalytic activity of an element in a system using and/or processing a fuel against impurities potentially present in the fuel, the method comprising the step of incorporating at least one protective additive in and/or on said element. Preferably, the fuel is suitable to be consumed by the fuel cell system

20

In a fourth aspect, the present invention provides a method of manufacturing a catalytically active element for a system using and/or processing a fuel, the method comprising the step of incorporating at least one protective additive in and/or on said element.

25

In a fifth aspect, the present invention provides the use of halogens or halide compounds for desensitising elements of solid oxide fuel systems against impurities.

30

Accordingly, the present inventors successfully used an additive in the preparation of a catalytically active element of a fuel processing system and surprisingly achieved a substantial protection of the catalytically active element against loss of catalytic activity due to impurities present in the fuel.

The present invention addresses particularly the presence in the fuel of impurities containing sulfur.

Brief Description of the Drawings

5

In the figures,

Figures 1 a and b show the effect of thiophene injection on current and impedance characteristics of a SOFC, where the cermet anode is *not* modified for sulfur tolerance: (1 a) current is plotted against time, the moment of sulfur injection is indicated (1); (2 b) impedance data, where the small semicircle in blue on the left side of the graph (2) presents the impedance of the anode before sulfur injection and the central and right-side, larger curves (in red) denote the impedance of the anode after sulfur poisoning.

Figure 2 shows the evolution of current as a function of time at a fixed voltage, with repeated injection of thiophene, for a SOFC containing a Ni-cermet anode desensitised in accordance with the present invention. Thiophene is injected repeatedly until the cell became deactivated (current falling to <0 mA). It was verified that this deactivation was due to carbon deposition since removal of the carbon by thermal treatment reactivated the cell. Thermal treatment does not reactivate a cell deactivated by sulfur but does reactivate a cell deactivated by carbon.

Figure 3 shows the cell performance as a function of time, after deactivation due to carbon deposits and reactivation. Reactivation was achieved by oxidation of the carbon in air at 500°C . The graph shows that sulfur impurities did not lead to a loss of catalytic activity.

25

Figure 4 shows a solid oxide fuel cell (SOFC) with Ni-cermet modified according to the present invention showing a stable operation under continuous H_2 fuel stream containing H_2S as the sulfur impurity vector. Again, this demonstrates that the invention completely prevents loss of catalytic activity due to sulfur.

30

Detailed Description of the Preferred Embodiments

The present invention relates to a system using and/or processing a fuel, the system comprising one or more elements having a catalytic activity. A system using and/or

processing fuel may be any system in which fuel is subjected to a chemical reaction. For example, a system processing fuel may be a sub-system of a larger system, the larger system having the purpose of converting fuel to any desired form of available energy. For example, a system processing fuel may be a reforming system, which performs the steam reforming of natural gas to produce carbon monoxide and hydrogen. The reforming systems operate with the aid of a catalyst. In general, the element having a catalytic activity is a catalyst, preferably a supported transition metal catalyst. For example, the transition metal may be selected from one or more of Ni, Ru, Cu, Au, Zn. These materials are preferably on a support, for example a support selected from alumina, silica, zirconium oxide, titanium oxide, others and combinations of the aforementioned.

Preferably, the system using and/or processing fuel is a fuel cell system. Accordingly, the system using and/or processing fuel is preferably an apparatus/device. A fuel cell system, according to the invention is a system in which the chemical energy of the fuel is converted to electrical energy and heat. Preferably, the fuel cell system comprises a solid oxide fuel cell (SOFC), which is a fuel cell using a solid ion conducting electrolyte. For example, the fuel cell system comprises a fuel cell comprising an anode, an electrolyte and a cathode. For example, the system is a fuel cell.

According to an embodiment, the system of the present invention has an operating temperature which is $\geq 140^{\circ}\text{C}$, preferably $\geq 400^{\circ}\text{C}$, even more preferably $\geq 600^{\circ}\text{C}$. Preferably, the system comprises and/or is a fuel cell, operating at the indicated temperatures.

The system of the invention comprises an element accomplishing a catalytic activity. This element may be an element of a solid oxide fuel cell. For example, in a fuel cell, the element having a catalytic activity may be the anode. The anode preferably comprises nickel (Ni). Preferably, the anode is a cermet, that is, a material comprising ceramic and metallic materials, in particular a composite material comprising ceramic and metallic materials. The catalytically active element may be an anode made of Ni-cermet. According to another embodiment, the catalytic element comprises a conducting oxide, for example a lanthanum chromite, in particular a lanthanum chromite, in which lanthanum is partially substituted with Ni. The catalytic element may comprise an ion-conducting oxide.

Specific materials for catalytic elements that are suitable for the present invention are disclosed, for example, by J. Sfeir, P. A. Buffat, P. Möckli, N. Xanthopoulos, R. Vasquez, H. J. Mathieu, J. Van herle and K. R. Thampi, "Lanthanum Chromite Based Catalysts for Oxidation of Methane Directly on SOFC Anodes", J. Catalysis 202 (2001), 229 ; and in
5 WO03005475 entitled 'Lanthanide chromite based SOFC anodes', J. Sfeir and K.R. Thampi.

According to an embodiment, where the catalytically active element is a cermet further comprising an ion-conductive oxide, the oxide comprises one or more selected from zirconium (Zr), cerium (Ce), gallium (Ga), and bismuth (Bi).

10

According to an embodiment, the catalytically active element is desensitised. Preferably, the catalytically active element of the present invention is one or more selected from a component of a chemical fuel processing subsystem, an electrochemical fuel processing subsystem, an interconnect, or a gas supply channel.

15

The fuel cell of the present invention is preferably a solid oxide fuel cell (SOFC). Alternatively the fuel cell is a molten carbonate fuel cell (MCFC).

As indicated above, the system may comprise an electrolyte. Electrolytes may be selected, for
20 example, from an oxygen ionic conductor, hydrogen ionic conductor, a carbonate ionic conductor or a combination of these.

According to the invention, the element having catalytic activity comprises at least one stabilising additive capable of desensitising said element. Preferably, the stabilising additive
25 protects the catalytic activity of said element in presence of impurities.

For the purpose of the present invention, the expression "protects the catalytic activity in presence of impurities" does not necessarily mean that a total protection is obtained and no loss of catalytic activity due to impurities at all is suffered. This expression rather expresses
30 that the additive has the effect of reducing loss of catalytic activity caused by the impurities, if compared to a catalytically active element devoid of said additive. Preferably, the additive has the effect of significant reduction of loss of catalytic activity. The additive thus has at least some measurable protective effect. While the present inventors found surprisingly high levels

of protective effect of the additive, the present invention also encompasses those instances, where only partial protection of catalytic activity is obtained.

5 The stabilising additive preferably comprises and/or consists of at least one non-metal element. According to an embodiment, the stabilising additive comprises a nonmetal of group VIIa or its compounds.

10 The stabilising additive thus preferably comprises, more preferably consists of, a halogen. The stabilising additive preferably comprises a halide. Preferred halogens are fluorine and/or chlorine.

15 The catalytically active element of the system of the invention may comprise at least one further stabilising (desensitising) additive. The further stabilising additive preferably is a metal, even more preferably a transition metal, and most preferably it is selected amongst one or more of Mo, W, Re, Rh, Os, Ir. For example, the protective metal may be introduced in the form of a soluble salt by infiltration of a solution into the porosity of a given anode, following the procedure disclosed by M. Smith and A.J. McEvoy, "Sulfur-Tolerant Cermet Anodes", SOFC IX, Quebec, Canada (2005); Proc. Vol. 2005-07, Electrochem. Soc., USA., p. 1437.

20 According to a preferred embodiment, at least one catalytically active element of the fuel processing system of the invention comprises a halide functioning as a protective additive against impurities possibly present in the fuel.

25 According to an embodiment of the present invention, the impurities are present in the fuel, and wherein the fuel is susceptible of being at least partially used in an energy conversion system, and wherein the impurities comprise sulphur in elemental or compound form.

30 Impurities, for the purpose of the present invention, comprise and/or consist of sulfur (S, S_n, sulfur in elemental form) and/or compounds containing sulfur (sulphur in compound form). The expression "sulfur in compound form" encompasses sulfur in all kinds of chemical compounds, such as H₂S and hydrocarbons containing sulfur atoms, such as thiophene, for example. It also comprises anorganic sulfur compounds, for example ammonium sulfide.

The stabilising additive may be added to the catalytically active element according to the methods of the present invention, directed to desensitisation of an element of a fuel processing system, to a method of making a catalytically active element, and/or to a method of protecting a catalytic activity of an element in a system using and/or processing a fuel, for example. Accordingly, at least one stabilising additive is preferably incorporated in and/or on said catalytically active element. The stabilising additive may be incorporated on the surface and/or in the bulk of the catalytically active element

Preferably, the stabilising additive is incorporated in and/or on the catalytically active element before exposure of the element to fuel comprising an impurity.

According to a preferred embodiment of the method of the present invention, the step of incorporating a stabilising additive in and/or on the catalytically active element preferably comprises one or more steps selected from:

- impregnating said element with at least one stabilising additive dissolved or suspended in a liquid;
- reacting said element with at least one stabilising additive provided in a gaseous and/or plasma phase; and
- incorporating at least one stabilising additive in said element prior to a high temperature sintering and/or reduction step.

The stabilising additive may be provided in a gaseous and/or plasma phase, in which case the catalytically active element may be exposed to the gaseous and/or plasma phase so as to react with the stabilising additive.

According to an embodiment, the step of incorporating at least one stabilising additive in and/or on said element is a processing method selected from ion implantation, vacuum plasma spraying, e-beam evaporation, air plasma spraying, and combinations including one or more from the aforementioned. If the stabilising additive is incorporated in and/or on said catalytically active element, for example, the stabilising additive may be provided in a gaseous and/or plasma phase so as to react it with the catalytically active element, a processing method may be selected from: ion implantation, vacuum plasma spraying, e-beam evaporation, air plasma spraying, and combinations including one or more from the aforementioned.

If the additive is incorporated prior to a high temperature sintering and/or reduction step, the stabilising additive may be incorporated during a process of fabrication of said catalytically active element. Accordingly, the element may from the beginning be manufactured incorporating the stabilising additive.

According to an embodiment, the protective additive is added by impregnation. In this case, the additive is preferably dissolved or suspended in a liquid, and the catalytically active element is impregnated with the solution and/or suspension. For example, halide-containing compounds, for example polymers containing halides or ammonium halides may be used. Preferably, the halide-containing compound is dissolved in a suitable solvent, for example an alcohol. Thereafter, the impregnating solution is applied to the catalytically active element, for example drop-wise. Thereafter, solvent is allowed to evaporate, and the application may be repeated, if necessary or desired. If the catalytically active element is heated, for example to a temperature of $\geq 50^{\circ}\text{C}$, before adding the impregnating liquid, the evaporation takes place more quickly. The catalytically active element may be a Ni-cermet anode of a solid oxide fuel cell. In this case, the impregnation may be carried out as exemplified in the example.

The present invention will now be illustrated by way of an example, which is by no means intended to limit the scope of the invention.

Example: Testing of modified Ni-cermet anode material for SOFC

Methods and Materials

SOFC anodes have been modified by impregnation with halides. Solutions of polymers containing halides, or of ammonium halides were used for impregnation.

First, cells with a Ni-cermet anode and a standard electrolyte of yttria-stabilised zirconia and a standard cathode made of lanthanum strontium manganite (LSM) are kept on a hotplate and heated to about 70°C . Up to 2 ml of a 5% solution of polyvinyl fluoride (PVDF) in alcohol is then allowed to slowly spread on the cermet anode by dropwise application of the solution. The alcohol is then allowed to evaporate, before adding more solution. Upon drying the cell is ready for mounting in the test rig. The test cells were YSZ electrolyte-supported, and

procured from several commercial manufacturers. Anode-supported cells were also tested, in the same manner.

For testing, a cell with or without impregnation is mounted in a test rig as described in J. Van herle and K. R. Thampi, "Laboratory techniques for evaluating solid oxide fuel cells", Journal of Applied Electrochemistry 24 (1994) 970-976, along with platinum mesh contacts and ceramic felt insulation materials. The cells were provided with independent voltage and current leads for measurements. The test rig was installed in a modified muffle furnace and is equipped with a thermocouple placed close to the working cell to measure the device temperature with all possible precision. H₂ fuel is admitted over the anode of the test cell after humidification by passing through a column containing 50-60 ml of water. This humidifier is provided with a septum to inject sulphur compounds. The cathode side of the fuel cell is fed with air, as the oxidant. The flow rates of both gases are controlled by appropriate flow meters. Each cell is slowly heated at 200 °C/h rate to the operating temperature under a steady flow of fuel and air streams (several decades to hundreds of milliliters/minute, depending on the cell active area). The organic part of the impregnated solution burns away during the heating process, and the resulting modified active anode is then ready for use. The data acquisition system for current/voltage and impedance measurements is a Solartron 1286/1255 electrochemical workstation. I-V curves were recorded by a Wenking Potentiostat, which can take up to 10A current load. Standard measurements were made at an operating temperature of 800°C. Besides the normal I-V and impedance characteristics, additional measurements were made by polarizing the cell at a constant potential such that the resulting when current is maintained close to 100 mA/cm². The current is then monitored as a function of time.

Injection of sulfur compounds into the fuel gas stream is done by either adding known amounts of thiophene to the humidifier as a second phase, which co-evaporates with the water, or by injecting it directly into the fuel feed close to the gas entry point leading to the anode. In some experiments, thiophene is replaced with H₂S as the source of sulfur. In this case, first a saturated solution of H₂S in water was prepared and a known amount of this is added to the humidifier. In experiments where sulfur is steadily admitted along with the fuel in a continuous manner, the supply of H₂S or thiophene is renewed periodically by adding fresh quantities, when the fuel stream shows a decline of H₂S concentration. In both cases,

where the sulfur compound is added to the humidifier, the feed rate of sulfide to the anode will be a function of the vapour pressure of thiophene or H₂S at room temperature.

The experiments have been done with both the modified and unmodified Ni-cermet anodes for comparison.

Results

Non-modified Ni-cermet anode

The effect of sulfur poisoning on an unmodified Ni-Cermet anode is shown in Figure 1, where the effect of sulfur on the current is observed at a fixed cell potential. The produced current is plotted negatively in the figure. The device is operated on humidified hydrogen fuel and sulfur is admitted in the form of thiophene (C₄H₄S), a volatile liquid used as an odorant natural gas supplies. A dose of 25 microlitres of thiophene is passed into the fuel stream, at a time indicated with reference numeral 1 in Figure 1 (a). While the thiophene was injected, the current started increasing first, due to the fact that thiophene can oxidise exothermally therefore acting as a fuel. The injection also causes a temporary change in the relevant gas pressure, but this is very brief. Subsequently, the current started to decrease rapidly to a very low value, indicating the expected irreversible damage occurring to the Ni-cermet anode. The cell became entirely deactivated due to the sulfur poison and it never recovered even after heating for many hours under pure hydrogen.

In Figure 1 (b) reference numerals 2 and 3 indicate impedance data before and after sulfur injection, respectively.

Ni-cermet anode according to the invention

Figure 2 shows a typical data for a SOFC containing an anode desensitised to sulfur/sulfides. The cell withstood repeated injection of thiophene for 6 times (up to 500 microlitres each time). In Figure 2, injections 1-6 are indicated with reference numerals 5, 6, 7, 8, 9 and 10, respectively. After each injection, the cell showed increased currents, which slowly came back to the original. However, after the sixth injection (10), the cell performance showed a

sudden decline and the current went below zero (reference numeral 11 in Figures 2 and 3). Simultaneously, the open circuit voltage also dropped to <500 mV, from the initial values of >1000 mV. This indicates a sudden deterioration of the cell. The reason for the observed breakdown of Ni-cermet anode function after 6 repeated injections of thiophene has been investigated. The cell on cooling showed a heavy deposit of carbon particles over its anode. This carbon originating from the thiophene, and the initial spike in current after each injection, together indicate that the organic thio-compound is able to function itself as a fuel, by providing the anode with CO and H₂ formed by cracking and limited partial reforming due to the presence of 3% water vapour in the humidified fuel feed. However, this low level of steam is not sufficient to completely prevent the carbon formation. This reasoning has been substantiated by the data shown in Figures 3 and 4. The anode of the cell after the run shown in Figure 2 is further subjected to oxidation in air at 500 °C (Figure 3, reference numeral 12), in order to burn off the deposited carbon. As expected, following restart (13) the cell regained its activity and could easily tolerate a further dose of 500 microlitres of thiophene (14). Then, a heavy dose of 1500 microlitres of thiophene followed (15), which deactivated the cell once again (16). V_{OC} at this moment was = 150mV. This data is shown in Figure 3. The cell, as before, showed a thick layer of carbon over the anode. XPS measurements showed mostly graphitic carbon on the surface. It is therefore established that the new and improved desensitisation catalyst very well protects the cermet against sulfur under these rigorous conditions; the degradation is due to the carbon formation, which can be expected with any unreformed carbon-based fuel. The state of the art as in previously published results (M. Smith and A.J.McEvoy, "Sulfur-Tolerant Cermet Anodes", SOFC IX, Quebec, Canada (2005); Proc. Vol. 2005-07, Electrochem. Soc., USA., p. 1437; M. Smith and A. J. McEvoy, "Regeneration of Anodes Exposed to Sulfur", Electrochemical Society Transactions, 7(1) 373, 2007) with HDS catalysts indicated a level of protection of the electrocatalytic properties of the cermet, but not the high level of protection against sulfur deactivation demonstrated by the present invention.

Figure 4 shows the performance of a SOFC with Ni-cermet desensitised to sulfur in accordance with the present invention over a long period (>300 hours) of operation, until the experiment was stopped. The fuel contained a continuous supply of H₂S. There was no evidence of sulfur-induced corrosion of the anode. Unlike thiophene, H₂S is a carbon-free sulfur source and hence the cell did not face any problem associated with carbon deposition.

A similar operation under a continuous supply of thiophene showed a trouble free operation for >40 hours, before failure due to heavy carbon formation.

Conclusion

5

This new method of desensitising Ni-cermet anodes is significantly more effective than any reported before, desensitising them to sulfur/sulfide in elemental or compound form, maintaining their necessary electrocatalytic performance and giving considerable protection against sulfur related chemical corrosion. This invention offers an easy method to operate fuel

10 cells with fuels containing sulfur impurities, thereby increasing reliability and decreasing operating costs by the elimination of a desulfurising subsystem, which otherwise represents significant capital and maintenance costs.

15

Claims

1. A system using and/or processing a fuel, the system comprising one or more elements having a catalytic activity, wherein the element comprises at least one stabilising additive
5 capable of protecting the catalytic activity of said element in presence of an impurity.

2. The system of claim 1, wherein the impurity is present in the fuel, and wherein the fuel is susceptible of being at least partially used in an energy conversion system, and wherein the impurities comprise sulfur in elemental and/or compound form.

3. The system of any one of claims 1 or 2, which is a fuel cell system.

4. The system of any one of the preceding claims, wherein the stabilising additive comprises a non-metal element.

5. The system of any one of the preceding claims, wherein the stabilising additive comprises a nonmetal of group VIIa and/or its compounds.

6. The system of any one of the preceding claims, wherein the stabilising additive
20 comprises fluorine and/or chlorine.

7. The system of any one of the preceding claims, wherein the element is an anode comprising Ni.

8. The system of claim 7, wherein the element is a cermet further comprising a
25 conducting oxide.

9. The system of claim 8, wherein the oxide comprises one or more selected from Zr, Ce, Ga and Bi.

10. The system according to any one of the preceding claims comprising a fuel cell having
30 an optimal operation temperature which is $\geq 140^{\circ}\text{C}$, preferably $\geq 400^{\circ}\text{C}$.

11. The system according to any one of the preceding claims, comprising a solid oxide fuel cell (SOFC).

12. The system according to any one of the preceding claims, wherein the element
5 comprising one or more stabilising additives is an element of a solid oxide fuel cell.

13. The system according to any one of the preceding claims, wherein the element comprising one or more stabilising additives is the anode of a solid oxide fuel cell.

10 14. The system according to any one of claims 3-10, wherein the fuel cell is a molten carbonate fuel cell (MCFC).

15. The system of any one of the preceding claims, comprising a further stabilising additive, said further stabilising additive being a metal.

15

16. The system of any one of the preceding claims, comprising a further stabilising additive, said further stabilising additive being a transition metal.

17. The system according to any one of the preceding claims, comprising an electrolyte
20 selected from an oxygen ionic conductor, a hydrogen ionic conductor, a carbonate ionic conductor or any combination of two or more of these.

18. A system according to any one of the preceding claims, wherein the element is one or more selected from a component of a fuel processing subsystem, an interconnect, or a gas
25 supply channel.

19. A method of desensitising an element of a system using and/or processing a fuel against impurities potentially present in the fuel, wherein the fuel is suitable to be consumed by the system, the method comprising the step of incorporating at least one stabilising
30 additive in and/or on said element.

20. The method of claim 19, wherein the step of incorporating at least one stabilising additive in and/or on the catalytically active element comprises one or more steps selected from:

- impregnating said element with at least one stabilising additive dissolved or suspended in a liquid;

- reacting said element with at least one stabilising additive provided in a gaseous and/or plasma phase;

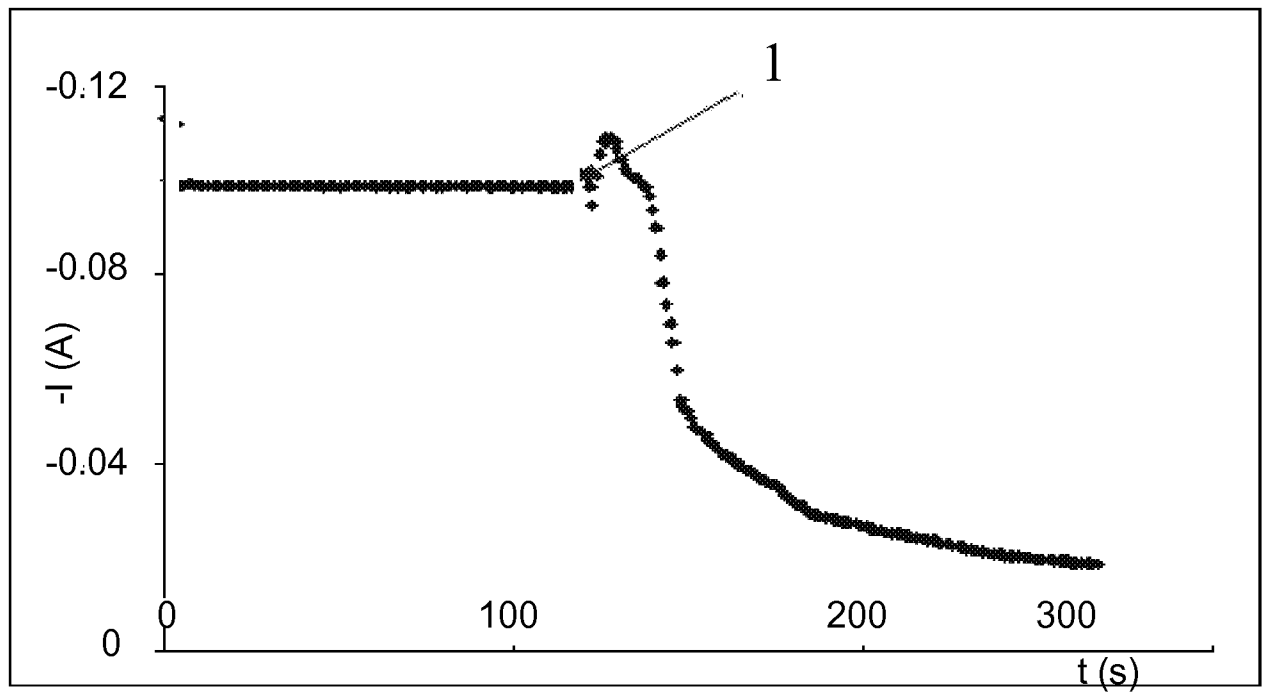
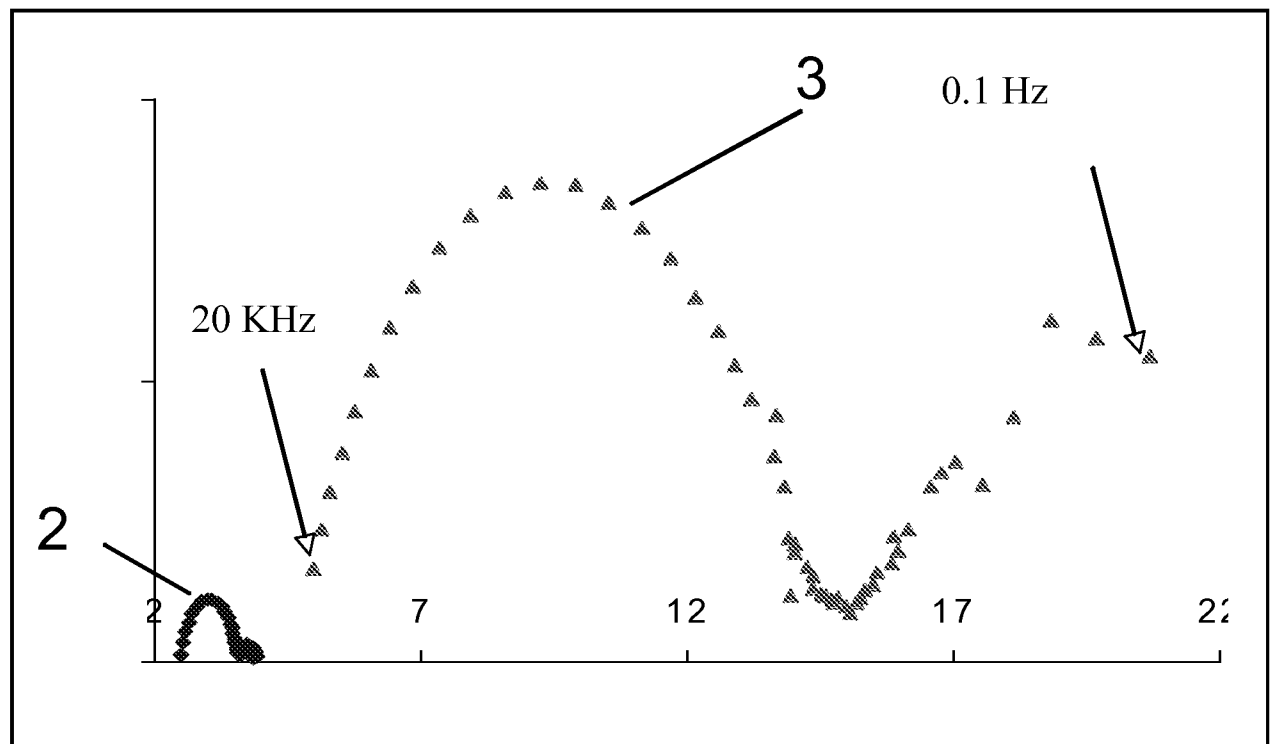
5 - incorporating at least one stabilising additive in said element prior to a high temperature sintering and/or reduction step.

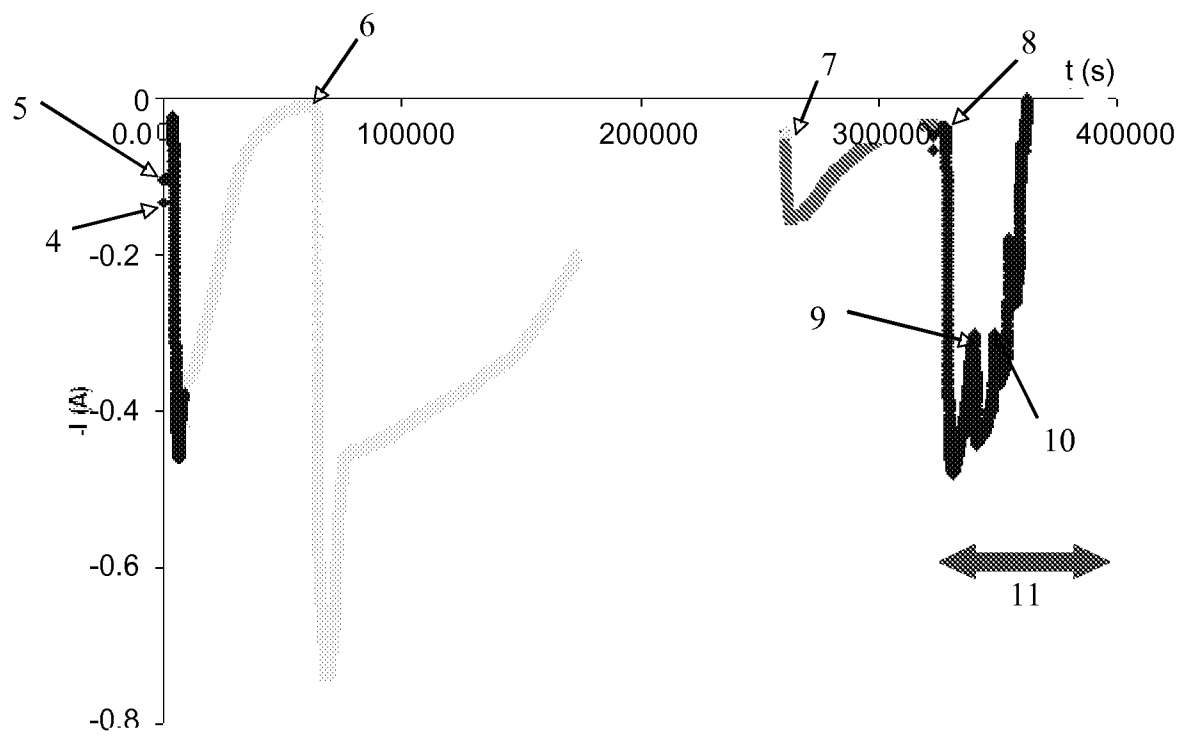
21. The method of claim 19, wherein the step of incorporating at least one stabilising additive in and/or on said element is a processing method selected from ion implantation,
10 vacuum plasma spraying, e-beam evaporation, air plasma spraying, and combinations including one or more from the aforementioned.

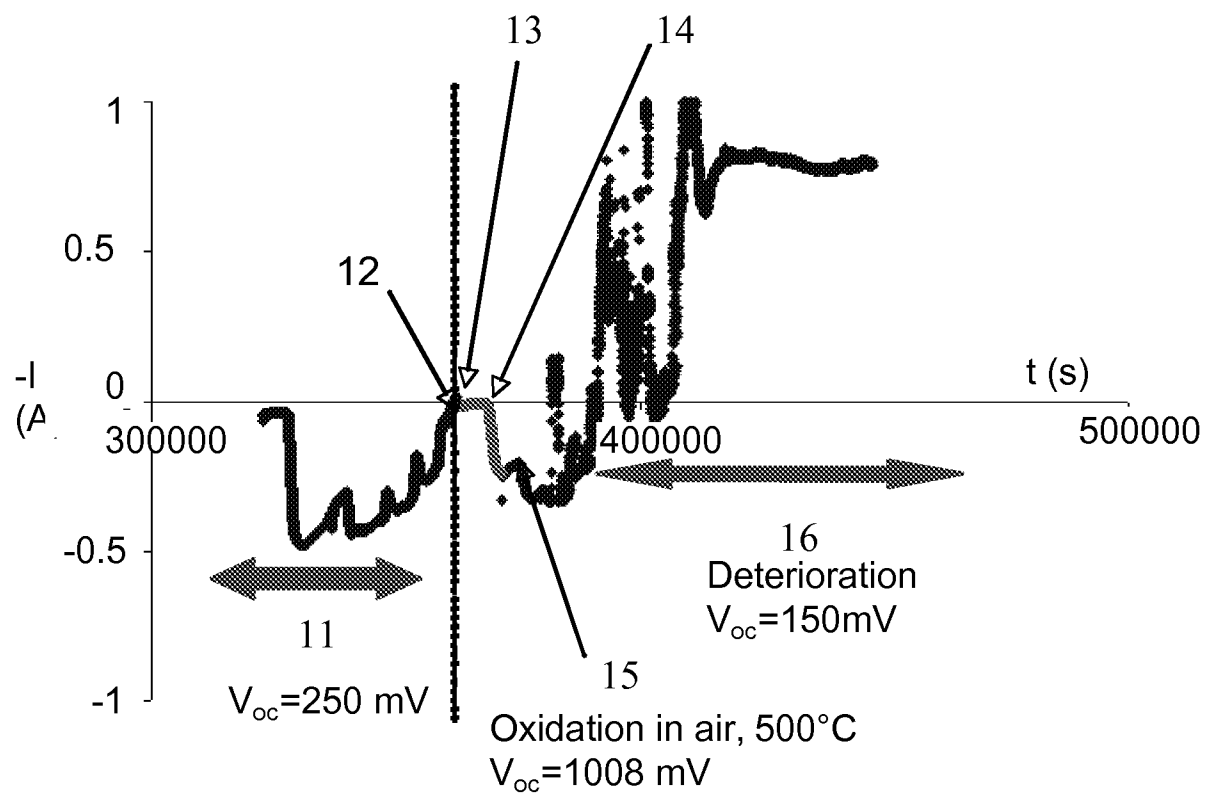
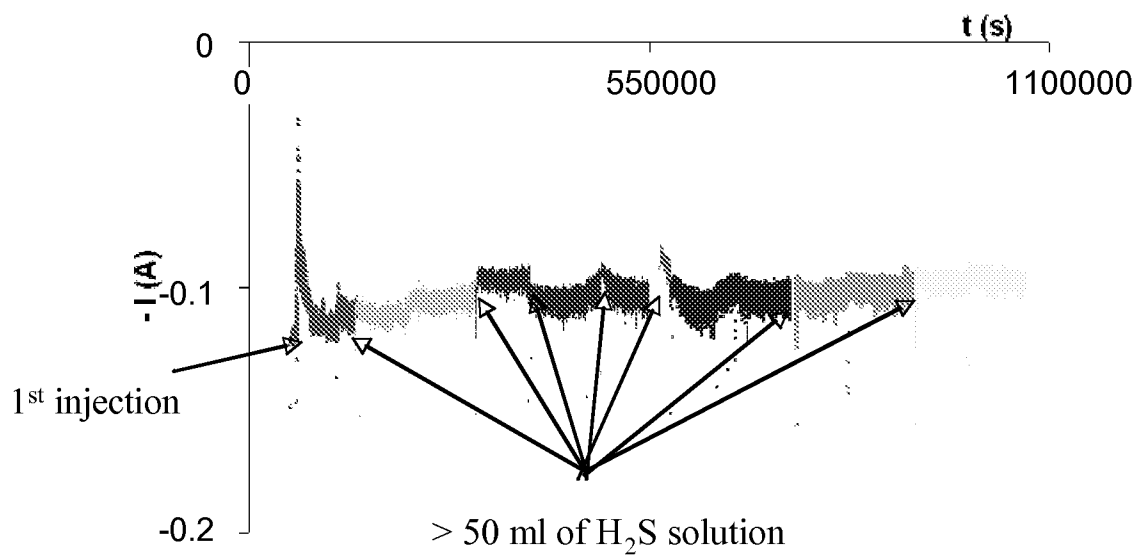
22. The use of halides or halide compounds for desensitising elements of solid oxide fuel cell systems against impurities.
15

23. A method of protecting a catalytic activity of an element in a system using and/or processing a fuel against impurities potentially present in said fuel, the method comprising the step of incorporating at least one protective additive in and/or on said element.

20 24. A method of making a catalytically active element for a system using and/or processing a fuel, the method comprising the step of incorporating at least one protective additive in and/or on said element.

**Figure 1 a****Figure 1 b**

**Figure 2**

**Figure 3****Figure 4**

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2008/050729

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01M4/90 H01M8/12 H01M8/14 H01M4/86 H01M8/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01M

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

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

EPO-Internal, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2008/008409 A (TRUSTEES OF THE UNIVERSITY OF [US]; GORTE RAYMOND J [US]; VOHS JOHN M) 17 January 2008 (2008-01-17) paragraphs [0003] - [0005], [0008], [0036], [0046], [0054] - [0056], [0064] - [0066]	1-4, 7-13, 15-18
X	WO 2006/125177 A (MASSACHUSETTS INST TECHNOLOGY [US]; YING JACKIE Y [US]; WEISS STEVEN E) 23 November 2006 (2006-11-23) pages 3,7 - page 21	1-3, 7-13, 15-19, 23,24
X	WO 2007/015391 A (JAPAN ENERGY CORP [JP]; TOIDA YASUHIRO [JP]; SAITO TORU [JP]) 8 February 2007 (2007-02-08) the whole document -/--	1-6, 14-16, 18-24

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

29 August 2008

Date of mailing of the international search report

04/09/2008

Name and mailing address of the ISA/

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

Authorized officer

Langouët, Sylvain

INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2008/050729

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	& EP 1 923 451 A (JAPAN ENERGY CORP [JP]) 21 May 2008 (2008-05-21) paragraphs [0001], [0007] - [0010], [0015], [0016], [0031], [0032], [0039], [0051] - [0053] -----	1-6, 15, 16, 18, 19, 22-24
A	JP 2001 279268 A (IDEMITSU KOSAN CO) 10 October 2001 (2001-10-10) the whole document -----	1-24

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2008/050729

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 2008008409	A	17-01-2008	US	2008090127 A1	17-04-2008
WO 2006125177	A	23-11-2006	NONE		
WO 2007015391	A	08-02-2007	EP	1923451 A1	21-05-2008
			KR	20080036123 A	24-04-2008
EP 1923451	A	21-05-2008	WO	2007015391 A1	08-02-2007
			KR	20080036123 A	24-04-2008
JP 2001279268	A	10-10-2001	NONE		