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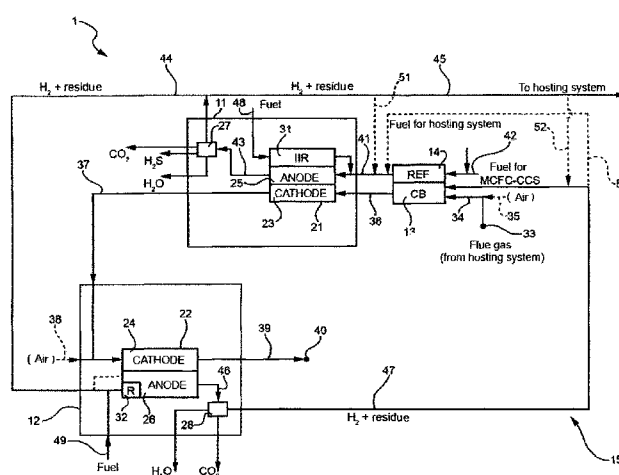
(54) Title: MULTI-STACK MCFC SYSTEM AND METHOD FOR SEPARATING CO₂ FROM COMBUSTION FLUE GAS CONTAINING SOX AND NOX

FIG. 1

(57) Abstract: A multi-stack MCFC system (1) for separating CO₂ from combustion flue gas containing NO_x and SO_x comprises: a first MCFC-CCS block (11) of MCFC stacks and at least a second MCFC-CCS block (12) of MCFC stacks, having respective separators (27, 28) acting on the anodic exhausts, at least one burner (13) and a connection system (15) that connects the blocks (11, 12) and the burner (13) so that: the cathodes (23, 24) of the stacks (21, 22) of the two blocks (11, 12) are connected in series; the flue gas to treat only enters into the cathodes (23) of the stacks (21) of the first block (11), with or without addition of air; in the second block (12), and in any following blocks, no flue gas enters that has not passed through the cathodes (23) of stacks (21) of the first block (11); the anodes (25, 26) of the stacks (21, 22) of each block (11, 12) are connected to respective separators (27, 28), that remove H₂O and separate a stream with CO₂ intended to be captured by a stream rich in H₂; the separators (27, 28) and the lines that manipulate the anodic exhausts are organized so that H₂S and N₂ are ejected from the system.



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MULTI-STACK MCFC SYSTEM AND METHOD FOR SEPARATING CO₂
FROM COMBUSTION FLUE GAS CONTAINING NO_x AND SO_x

TECHNICAL FIELD

5 The present invention relates to a multi-stack MCFC system for separating CO₂ from combustion flue gas containing NO_x and SO_x, and to a method for separating CO₂ from combustion flue gas containing NO_x and SO_x by means of a multi-stack MCFC system.

10 In particular, the invention relates to the field of systems for separating CO₂ from combustion flue gas, and more specifically to the field of processes and devices capable of selectively extracting CO₂ from the flue gas it is diluted into, in order to provide it
15 concentrated in a gaseous stream from which it can be easily separated. Even more specifically, the invention relates to the field of MCFC-CCS systems, i.e. systems where by means of molten carbonate fuel cells (MCFC), CO₂ is extracted from the flue gas it is diluted into
20 and is concentrated in a gaseous stream rich in H₂O vapor and substantially free from diluting N₂, so as to facilitate the subsequent capture thereof (CCS = "Carbon Capture and Storage").

BACKGROUND ART

25 The capability of molten carbonate fuel cells (MCFC) systems of carrying out the separation of CO₂

from combustion flue gas supplied to the cathode is known. Several system layouts have been suggested, with both pressurized and atmospheric pressure solutions.

The capability of MCFC cells of extracting CO₂ from the cathode gas and release it into the anodic gas results indeed from the same operating principle of the cells; however, it is normally necessary, in order to provide efficient CCS systems, to manipulate the anode output gas prior to the CO₂ separation.

Various method of manipulating the anode exhaust are known so as to obtain, in addition to the CO₂ stream to be "captured" or used, also recovery H₂O and residual fuels to be used, as also a plurality of different methods are known to recover energy and/or products obtained through such a manipulation, within the MCFC-CCS system or for external uses.

It is also known to use both mono-stack MCFC systems and multi-stack MCFC systems to these ends.

In almost all multi-stack MCFC systems designed for distributed generation (currently almost the only field of application of MCFC cells), all the stacks are in parallel for both the anode and cathode supply, and are in the same nominal working conditions.

However, within this scope, MCFC systems have also been suggested where the stacks have the cathode supply, the anode supply or both supplies in series (as shown

for example in EP442352, US5413878, EP0947022), according to logics aimed to meet specific needs on a case by case basis, usually related to the increase in efficiency or improvements to thermal management. In any case, these are solutions designed for systems where all the CO₂ built up at the anode outlets is sent to the cathodes since it is required for the cathode supply within the same MCFC system, which circumstance actually leaves no margin for an extraction and capture thereof.

10 In said systems, in the practice, all the circulating CO₂ is released to the atmosphere through one or more cathode outlets.

In addition to MCFC systems with two or more stacks in fluid series, hybrid multi-stack systems are also known in the art, meaning that they incorporate fuel cells of a different line in a fluid series connection (as shown for example in US6033794, US6623880, US5541014).

As regards known MCFC-CCS systems, even when configured as multi-stack (i.e. consisting of multiple MCFC cell stacks electrically connected to one another), they are described as consisting of identical stacks, or all fluidly arranged in parallel, or organized as strings fluidly arranged in parallel, with each string consisting of two or more stacks in a series, and they are supplied so that the stacks (if all in parallel) or

all the strings of stacks, respectively, work in the same nominal process conditions. In the first case, the manipulating members of the anode exhausts may be one for each of the single stacks or in any case for multiple stacks; in the second case, one for every single string, a common one for multiple strings, or also one for single stacks of a string, as indicated in patent application MI2009A002259.

Therefore, the manipulation members of anode exhausts may be one for each of the single stacks in parallel, a common one for multiple stacks of a same string or also one common to multiple strings.

Even when the described solutions consist of strings of two (or more) stacks in a series, each provided with its own member for manipulating the anode exhaust, no solutions are known that provide differentiated recirculation paths for the different stacks of a string for the streams rich in H₂ collected in output from said members, so that through such a differentiation, the H₂ enrichment and H₂ use reduction effects that can be obtained by the same recirculation are concentrated on the first one of the stacks in a series along the string.

It is also known that several critical contaminants exist for MCFC and that each of them must remain below a specific threshold thereof, which leads

to limitations to their contents in both the anode supplies and the cathode supplies.

Such limitations are significantly different also depending on the specific type of stack with direct
5 internal reformer (DIR), indirect internal reformer (IIR), without internal reformer (with external reformer, with H₂, syngas, biogas supply, etcetera).

The combustion flue gas may be very different by type and level of critical contaminants found, but they
10 usually have in common the fact of having some above the thresholds allowed by MCFC (sometimes well above them).

Therefore, in order to be conveniently usable, almost all the known MCFC-CCS systems require an adequate flue gas clean up to be arranged upstream, with
15 reference to the specific type of stack selected.

For this reason, direct internal reformer stacks (both in the base version, DIR and in that known as Advanced Internal Reformer, AIR), at present the best ones and most used in distributed generation, are not
20 considered conveniently usable for making the entire MCFC section of an MCFC-CCS system therewith since they would require an almost prohibitive flue gas cleaning (in particular, the SO_x contents must be restored to levels typically found in the air).

25 Also, the background art describes multi-stack MCFC-CCS systems that use DIR stacks as backbone for the

capture of CO₂ from the flue gas (and for producing electrical power with high efficiency associated thereto) and which nevertheless are suitable for accepting higher SO_x contents in input. In fact stacks
5 without direct internal Reformer are also found in such multi-stack systems, the cathodes of which are the only inlet way of the flue gas into the same MCFC-CCS system. DIR stacks are operated on dirty flue gas at the inlet of the MCFC-CCS system by having the cathode supply
10 downstream of a stack without DIR which, in addition to a complementary role in capturing CO₂, carries out a filtering action (Italian patent application MI2009A002259).

For such a system, the limits to SO_x are those
15 (much milder) valid for stacks with indirect internal reformer or without internal reformer and not the very restrictive ones required by DIR stacks.

In fact, the S found in the flue gas (in the form of SO_x) is almost integrally captured by the electrolyte
20 of the first stack that encounters on its path (and then released as H₂S in the anode exhaust of said stack). Since in the solution described in MI2009A002259 this first stack is not provided with direct internal reformer, the thermal management and the H₂ availability
25 therein are not affected by the release as H₂S in the anode compartment of SO_x entered on the cathode side.

SOx is absent in the supply of the DIR stack cathodes and therefore the vitality of catalyst, directly arranged into the anode compartment, is not affected.

In stacks without DIR, those which are crossed by
5 the flue gas entering into the MCFC-CCS system, the release of H₂S into the anode gas that flows towards the outlet does not produce a drift towards an irreversible degradation, as on the other hand would happen if they were DIR stacks. Thus, the SOx entered into the cathode
10 can be ejected as H₂S without any destructive effects on the cell efficiency. Of course (if SOx exceeds the valid threshold for stacks of the specific type used) there is a penalization of the performance, which also causes a decrease in the current density at which such a stack
15 can work compared to operations with clean gas. In any case, it is possible to keep a steady working point, unless an excessive threshold excess is required to be achieved, which also in this case would trigger a degradation mechanism.

20 While MI2009A002259 only relates to the arrangement in series of a stack without DIR and of a DIR, the teaching that can be derived therefrom is wider: placing two stacks in a series on the cathode side makes the downstream one work with cleaner oxidant
25 and without SOx.

The SOx level in the cathode being the same, the

penalization extent is very sensitive to the composition and use of the anode gas: gases rich in H₂ and low H₂ use reduce it.

It is also known that recirculating at the anode inlet the stream with the residue rich in H₂ exiting from the separator that removes H₂O and extracts CO₂ from the anode exhaust allows the efficiency of the MCFC-CCS system to be increased (as described for example in US7396603), since, without making the cell voltage fall down, it allows the limit to be brought up to 100% the percentage of hydrogen introduced from the outside (or derived from fuel supplied from the outside) which is used in generating current. In fact, in order to suitably increase the flow rate of such a recirculation, it is possible to restrain within the desired limits the so-called "use of H₂ at the stack level", i.e. that calculated as ratio between the H₂ flow rate used for producing current and H₂ flow rate that globally enters into the anode, including the recirculation.

In general, the known system configurations (in particular, mono-stack or multi-stack ones with stacks in parallel only and without anode recirculation) unavoidably require an additional strong clean up.

In particular, the SO_x contents must be brought below the valid threshold when the specific type of

stack used works with poor anode gas.

In fact, such systems cannot but entrust the entire current generation, with which the capture of CO₂ is associated, to stacks in which the flue gas enters directly. Moreover, a high electrical efficiency cannot be reached without a large use of fuel and in such systems, a large use of H₂ automatically implies an impoverishment of the gas in the entire cell portion close to the anode outlet. Therefore, the sensitivity to SO_x for such stacks is high and the additional clean up cannot be but suitably strong.

The solutions that add the simple recirculation at the anode inlet of a portion of the anode exhaust as is (such as for example some solutions shown in EP0418064) worsen the problem.

In substance, in order to produce power with a high efficiency, most of the known MCFC-CCS systems have to impoverish the anode gas at least in the cell portion close to the outlet, and thus they require very strict thresholds on the SO_x and NO_x levels in the supplied flue gas.

The correction of this flaw through the recirculation at the anode inlet of the stream rich in H₂ exiting from the device that extracts CO₂ from the anode exhaust generates build up mechanisms that accentuate the SO_x and NO_x poisoning dynamics,

respectively. If the H₂S build up deriving from SO_x can be prevented with an appropriate selection of the CO₂ separator device installed on the anode exhaust, the only defense from NO_x (besides their removal from the
5 flue gas) is to change approach for enriching the anode gas.

The NO_x found in the cathode gas in fact tend to react with the electrolyte, forming alkaline nitrites and nitrates that are diffused in the die. The anode
10 side removal by the effect of the anode gas, much more effective when the anode gas is richer in H₂, takes place almost entirely generating N₂ and in a minimal part NH₃ (ratio in the order of 100:1).

As with SO_x, also NO_x cause a penalization of the
15 performance, so also in this case a steady working point can only be obtained at reduced current density and with a lower voltage than would be found in the same conditions with clean gases.

Trapping N₂ in the anode loop would unavoidably
20 inhibit the wash off, on the anode side, of nitrites and nitrates formed in the electrolyte by the effect of the cathode reaction with the NO_x. This would force the NO_x in the flue gas to be of few ppm, so as not to affect the stack efficiency.

25 Moreover, as a side effect, interrupting the NO_x drainage by the electrolyte, the N₂ build up would

prevent the use of the same stacks as an instrument for further reducing the NO_x emissions to the atmosphere by the hosting system, making the capability that is intrinsic to the MCFC but strictly related to the onset
5 and the persistence of anode side washing conditions, of converting a significant portion of the NO_x entered on the cathode side into N₂, useless.

DISCLOSURE OF INVENTION

It is an object of the present invention to
10 provide a system and a method for separating CO₂ from combustion flue gas by means of multi-stack molten carbonate fuel cells (MCFC) which is free from the drawbacks of the prior art mentioned above; in particular, it is an object of the invention to provide
15 an MCFC-CCS system which, compared to known systems, works at a high electrical efficiency and at the same time with higher thresholds on SO_x and NO_x in the cathode gas.

The present invention therefore relates to a
20 system and a method for separating CO₂ from combustion flue gas by means of multi-stack molten carbonate fuel cells (MCFC) as defined in essential terms in the annexed claims 1 and 12, respectively, as well as, for the preferred additional characters, in the dependent
25 claims.

In the practice, the main features of the

invention are as follows:

- the MCFC-CCS system is organized into two or more blocks of stacks, blocks having the respective cathode lines connected in series;

5 - the flue gas to be treated, containing contaminants, only enter into the cathodes of the stacks of the first block;

- the anodes of the stacks of the first block are made to operate as much as possible in excess of H₂, making as much H₂ as possible pass through them than what is globally required for supplying the entire MCFC-CCS system as a whole, optionally adding more H₂ that can be used by the hosting system or by other users;

- this way, the stacks of the first block can work with rich anode gas in input and with low use of H₂, and thus with rich gas (anode exhaust) in output too; this condition, for a given level of SO_x and NO_x, respectively, in input minimizes the performance penalization of the stacks of the first block with respect to those obtainable in the same working points with clean gases and at the same time it maximizes the capability of draining SO_x and NO_x from the flue gas supplied to the cathodes;

- this allows the following to be transferred into the anode exhaust of the stacks of the first block: in the form of H₂S, almost all the sulfur entered as SO_x on

the cathode side, and in the form of N₂, most of the NO_x entered on the cathode side;

- the separation devices for CO₂ recovery, located on the anode outputs of the stacks of the various blocks, and the lines that manipulate the anode exhaust are organized so that said H₂S and N₂ can be expelled from the MCFC-CCS system without making H₂S generated by the SO_x found in the flue gas pass in the anodes of the stacks of the second block (and of the following ones);

- by the effect of the above devices, the stacks of the blocks following the first one work on substantially clean oxidants, at most containing NO_x residues brought again below the thresholds that affect performance.

The main component elements of the invention therefore are:

a) an MCFC-CCS comprising at least two blocks of MCFC stacks (there are no bars for the type of stacks which may for example be of the DIR type, IIR type, without internal reformer, etcetera);

b) a connection system configured so that:

- the flue gas to treat with the MCFC-CCS system only supplies the cathodes of the stacks of the first block (with or without addition of air); the following blocks are only supplied with flue gas that has already passed through the cathodes of stacks of the first

block;

- the various blocks are in fluid connection in series on the cathode side, i.e., the outputs of the stack cathodes of the first block supply cathodes of the stacks of the second block (with or without addition of
5 air) and if the blocks are more than two, the outputs of the stack cathodes of the second block supply (with or without addition of air) cathodes of the stacks of the third block and so on, for any following blocks;

10 c) separator devices, connected to the anode outputs of all the cells of the stacks of all blocks and that remove H₂O and separate a stream containing CO₂ for the capture from a stream rich in H₂; said separator devices are organized so as:

15 - process the anode exhausts of the stacks of the first block removing H₂O, extracting CO₂ and at the same time also removing H₂S, in particular up to have an H₂S residue below 10% of the H₂S level found at the anode output; in this way, the stream rich in H₂ remains
20 substantially free from H₂S (or in any case it has a sufficiently low H₂S content); and

- at least one portion of the stream rich in H₂ exiting from the separator device connected on the anode outputs of the stacks of the first block is conveyed,
25 directly or after passing through the anodes of stacks of one or more of the other blocks, to a burner which

may be internal or external to the MCFC-CCS system; in this way, build-up phenomena of N₂ are prevented;

- at least one portion of the fuel required by other blocks, by the hosting system or by other external users passes, in the form of H₂, through the anodes of the stacks of the first block or alternatively, at least one portion of the stream rich in H₂ exiting from separator devices connected on the anode outputs of stacks of other blocks passes through the anodes of the stacks of the first block (and thus through the separator connected to the anode outputs of the stacks of the first block) before reaching the system internal or external burner.

The system as a whole is therefore configured to increase the H₂ content in the anode gas of the stacks of the first block (in input but also in output), without causing fuel wastes.

In addition to the general advantage, common to CO₂ separator systems working with MCFC cells, of separating CO₂ producing energy rather than using it (as it happens in conventional separator systems, all of the passive type), the invention achieves the following specific advantages compared to MCFC-CCS systems made according to the prior art.

Firstly, the present invention is capable of keeping the current generation mechanism in the MCFC

system active, which leads to the removal of CO₂ from the combustion flue gas, in spite of input SO_x and NO_x contents higher than those set as thresholds for known solutions.

5 It should be noted that the devices adopted according to the invention are simultaneously effective against NO_x and SO_x.

At the same time, the present invention allows the actual use of the potential of MCFC cells to act as an
10 instrument for reducing the emissions of residues not just of CO and SO_x but also of NO_x found in the flue gas.

Therefore:

- compared to the known solutions consisting of a
15 single stack or multiple stacks, all in parallel, without anode recirculation or with anode inlet recirculation of a portion of the anode exhaust drawn upstream of the separator, the invention achieves: the efficiency being the same, higher thresholds of both SO_x
20 and of NO_x contents in the flue gas; and SO_x and NO_x levels being the same, higher efficiency;

- compared to the known solutions consisting of a single stack or multiple stacks all in parallel, with anode inlet recirculation of the stream rich in H₂
25 exiting from the separator, the invention achieves much higher thresholds on NO_x and capability of using the

same stack as a further instrument for removing NO_x;

- compared to the solution with stacks in fluid series along the cathode lines (as that described in MI2009A002259), the invention achieves much higher
5 thresholds for both SO_x and for NO_x, along with a wide freedom in the selection of the type of stacks to make the blocks of the MCFC-CCS system.

More freedom in the selection of the type of stacks allows adequate responses to changes in priority
10 between higher performance requirements on shorter life spans and longer duration.

BRIEF DESCRIPTION OF THE DRAWINGS

Further features and advantages of the present invention will appear clearly from the following
15 description of a non-limiting embodiment example thereof, made with reference to the figures in the accompanying drawings, in which:

- figure 1 shows a schematic view of a system for separating CO₂ from combustion flue gas by means of
20 molten carbonate fuel cells (MCFC) made according to a first embodiment of the invention;

- figure 2 shows a schematic side view of a second embodiment of the invention;

- figures 3 and 4 show partial schematic views of
25 further variations of the system of the invention.

BEST MODE FOR CARRYING OUT THE INVENTION

With reference to figure 1, a system 1 comprises:
a first MCFC-CCS block 11 of MCFC stacks, at least a
second MCFC-CCS block 12 of MCFC stacks, at least one
5 burner 13 provided with reformer 14, and a connection
system 15 that connects blocks 11, 12 and burner 13.

While herein and in the following description
reference is made to a single second block 12, it is
understood that system 1 may include a series of second
10 blocks 12.

Blocks 11, 12 comprise respective groups of stacks
21, 22 of MCFC cells, having respective cathodes 23, 24
(or cathode compartments) and anodes 25, 26 (or anode
compartments), and respective separators 27, 28 acting
15 on the anode exhaust of stacks 21, 22. Cathodes 23, 24
of the two blocks 11, 12 are connected in series; if
multiple second blocks 12 are provided, they have the
cathodes of the respective stacks connected in series.

Preferably, stacks 21, 22 of both blocks are
20 provided with internal reformer 31, 32, for example
indirect (IIR) or direct (DIR) internal reformer.

System 1 has a flue gas inlet 33, through which
the combustion flue gas to be processed coming from a
hosting system and generally containing SO_x and NO_x,
25 enter into system 1.

In the example shown in figure 1, the flue gas

inlet 33 is arranged upstream of burner 13 and is connected to burner 13, which for example is a catalytic burner, via a flue gas supply line 34, through which the flue gas enters into burner 13; reformer 14 for example
5 is a MIR ("modular integrated reformer").

Optionally, air is added to the flue gas supplied to system 1, through an air supply line 35 which fits onto the flue gas supply line 34.

Burner 13 has an outlet connected to cathodes 23
10 of stacks 21 of the first block 11, through a cathode inlet line 36; cathodes 23 are therefore supplied with oxidizing gas consisting of the flue gas coming from the hosting system, optionally enriched with air and with the combustion products into burner 13.

15 The outlet of cathodes 23 is connected through a cathode line 37 to the inlet of cathodes 24 of stacks 22 of the second block 12. Optionally, an air supply line 38 fits onto the cathode line 37 for adding air to the stream supplied to cathodes 24. The stream exiting from
20 cathodes 24 is collected by a venting line 39 which leads to a vent 40.

Anodes 25 of the first block 11 are supplied with a stream coming from reformer 14 through an anode inlet line 41; reformer 14 is supplied with fuel through a
25 fuel supply line 42, for example CH₄, and with a flow rate of H₂O (vapor) needed for converting the fuel into

H₂. Advantageously, the fuel flow rate supplied to reformer 14 serves for covering all the uses of blocks 11, 12 (if only stacks without internal reformer are used) or the part in excess to that already covered by the hydrogen produced into the stacks (if stacks with internal reformer are provided) and also for supplying a fraction of the energy of the hosting system.

The streams exiting from anodes 25 of stacks 21 of the first block 11 are sent, through an anode line 43, to separator 27 (of the known type), configured so as to remove H₂O and extract CO₂ and H₂S, in a sequence or concurrently.

The stream rich in H₂ and containing residual fuels exiting from separator 27 is partly sent to anodes 26 of stacks 22 of the second block 12, through a further anode line 44 (either directly or passing through reformer 32), and partly to the hosting system, through an anode outlet line 45, to be used therein.

The streams exiting from anodes 26 of stacks 22 of the second block 12 are sent, through an anode line 46, to separator 28 (of the known type) which removes H₂O and extracts CO₂. The stream rich in H₂ and containing residual fuels exiting from separator 28 is sent through a recirculation line 47 to burner 13, where the residual fuels contained in such a stream are burnt and the heat is recovered for supporting the reactions within

reformer 14 and for heating the oxidizing gas containing the combustion flue gas supplied to the first block 11 (optionally, the flue gas is preheated through thermal exchange with the stream exiting from cathodes 24 of the second block 12). The conversion into H₂ of a fuel flow rate in excess of the requirement of the first block takes place within reformer 14, i.e. upstream of anodes 25 of the first block 11.

An additional flow rate of H₂ is thus generated that can pass unaltered through anodes 25 of the first block 11, contributing to reduce the use of H₂ and thereby to increase the output H₂ percentage too. This contributes to creating more favorable conditions for the removal of sulfur and nitrites/nitrates from the electrolyte. It should be noted that this happens without the need for additional fuel since a part of the fuel used by the hosting system is used without consuming it.

The internal reformers 31, 32 of stacks 21, 22 are supplied through respective fuel supply lines 48, 49 with fuel (CH₄) and vapor flow rates needed for allowing the thermal management of the respective stacks 21, 22, through the heat absorption associated with the endothermic reaction of H₂ production from the fuel reforming. The H₂ streams produced within reformers 31, 32 are supplied to anodes 25, 26 of the respective

stacks 21, 22.

The remaining portion of H₂ required for completing the overall H₂ requirement of stacks 21, 22 is produced within reformer 14, starting from fuel (CH₄) and vapor introduced through line 42.

The H₂ flow rate generated within reformer 14 by the conversion of the fuel introduced through line 42, adding to the H₂ flow rates generated within the internal reformers 31, 32 of stacks 21 of the first block 11 and of stacks 22 of the second block 12, covers the H₂ requirement needed for stacks 22 of the second block 12 to work at the desired current with the desired use of H₂, once the quantity of H₂ used into stacks 21 of the first block 11 for generating the desired current and that sent to the hosting line through line 45 has been subtracted.

Since reformer 14 is arranged upstream of anodes 25 of the first block 11, all the hydrogen generated within system 1, with the exception of that strictly necessary to generate within the internal reformer 32 of stacks 22 of the second block 12 for ensuring the thermal management thereof, enters into anodes 25 of stacks 21 of the first block 11. This is essential for enriching with H₂, both in input and in output, the anode gases of stacks 21 of the first block 11 to the maximum extent allowed, the fuel flow rate supplied to

system 1 being the same. In this way, it is possible to create the most favorable conditions for removing sulfur and nitrites/nitrates from the electrolyte into stacks 21 of the first block 11, while minimizing the impact of SOx and NOx on the performance, and to allow stacks 22 of the second block 12 to work with significantly reduced contents not only of SOx but also of NOx.

The devices used for enriching the anode gas of stacks 21 of the first block 11 are effective since they do not trigger build-up mechanisms of H₂S (which is removed by separator 27) or of N₂ (which is partly eliminated through the anode exit line 45 and partly through the venting line 39).

It is clear that several changes and variations may be made to the general layout described herein, especially as regards the ways for enriching the anode gas in H₂.

For example, according to a variation, the entire stream rich in H₂ exiting from separator 27 of the first block 11 is sent to anodes 26 of stacks 22 of the second block 12, through the anode line 44 (whereas the anode exit line 45 shown in figure 1 is not used).

According to a further variation, the stream rich in H₂ exiting from separator 27 is not sent to anodes 26 of stacks 22 of the second block 12, but it is partly sent to the hosting system, through the anode exit line

45, to be used therein, and it is partly recirculated through an anode recirculation line 51 (shown with a dashed line in figure 1) which fits onto the anode inlet line 41, to anodes 25 of stacks 21 of the first block 11 (whereas the anode line 44 is not used).

According to further variations, the stream rich in H₂ exiting from separator 27 is partly recirculated to anodes 25 of stacks 21 of the first block 11, through the anode recirculation line 51, and for the remaining part to burner 13, reaching it either through the recirculation line 47, after having passed through anodes 26 of stack 22 and through separator 28 of the second block 12, or directly through a further recirculation line 52 (also shown with a dashed line in figure 1) which fits onto said line 47, and/or to an external user (for example the hosting system), either directly or after passing through anodes 26 of stack 22 of the second block 12 (or of following blocks, if provided).

According to a further variation, the streams rich in H₂ exiting from separators 28 of the second block 12 are entirely or partially sent (rather than or in addition to burner 13) to anodes 25 of stacks 21 of the first block 11, through an auxiliary line 53 that branches off the recirculation line 47 and fits onto the anode inlet line 41, before being sent to burner 13 (or

another burner, internal or external to the MCFC-CCS blocks 11, 12), or to an external user.

In general, burner 13 may be internal or external to the MCFC-CCS blocks 11, 12.

5 Of course, further combinations of the described configurations may be used.

In any case, the flue gas passage in burner 13 favors the heating of the oxidizing gas to the inlet temperature to the stacks.

10 Of course, the flue gas heating may also be carried out in a different way, for example by recovering heat, with suitable exchangers, from one or more of the hot streams circulating within system 1 and that need to be cooled (such as for example the stream
15 exiting from cathodes 24 of the second block 12 and collected by the venting line 39, or the anode discharges exiting from anodes 25, 26 through the anode lines 43, 46).

In the examples described so far, the outlet of
20 burner 13 where the combustion of residual fuels not used by stacks 21, 22 of blocks 11, 12 takes place, is connected to cathodes 23 of stacks 21 of the first block 11, which are therefore supplied with the gaseous stream exiting from burner 13.

25 As an alternative, as shown in figure 2, in order to increase the capture of CO₂, system 1 comprises a

supplementary MCFC group 55, consisting of one or more stacks 56 of MCFC cells having respective cathodes 57 and anodes 58, and the outlet of burner 13 is connected to cathodes 57 of group 55, so that the gaseous flow exiting from burner 13 supplies cathodes 57 (optionally enriched with air).

Group 55 has an anode outlet connected, via an anode line 60, to a separator 59 that removes H₂O and CO₂ from a residual stream containing H₂.

10 In this case, the combustion flue gas coming from the hosting system is supplied, rather than to burner 13 as described above, to cathodes 23 of stacks 21 of the first block 11 (optionally after adding air through the air supply line 35). The flue gas inlet 33 is placed upstream of cathodes 23 and the flue gas supply line 34
15 directly enters into the first block 11 and supplies cathodes 23.

The fuel supply line 42 supplies, in addition to reformer 14 as described above, also anodes 58 of the supplementary group 55.
20

As regards the rest, system 1 still has the general configuration described above and the variations already mentioned with reference to figure 1 are possible, especially as regards the management of the stream rich in H₂ and containing residual fuels exiting from separator 27 of the first block 11, which may be
25

sent to one or more of:

- anodes 26 of stacks 22 of the second block 12, through the anode line 44 (either directly or passing through reformer 32);
- 5 - the hosting system, through the anode exit line 45;
- anodes 25 of stacks 21 of the first block 11, through the anode recirculation line 51;
- burner 13, through the recirculation line 52
- 10 that branches off the anode exit line 45 and fits onto the recirculation line 47 coming from anodes 26, after passing into separator 28 of the second block 12.

According to a further variation, the streams rich in H₂ (and containing residual fuels) exiting from

15 separator 28 of the second block 12 is partially sent directly to burner 13 through the recirculation line 47, and partially also to anodes 25 of stacks 21 of the first block 11, through an auxiliary line 53 that branches off line 47 and fits onto the anode inlet line

20 41 (that connects reformer 14 to anodes 25) before being sent to burner 13 (or another burner, internal or external to the MCFC-CCS blocks 11, 12), or to an external user.

According to a further variation (not shown) bases

25 on the general layout of figure 2, the stream exiting from burner 13 is also sent to the inlet of cathodes 24

of stacks 22 of the second block 12, and/or, in the case of multiple blocks 12 in series, of the cathodes of the stacks of one of the following blocks.

Further variations capable of further enriching the anode gas of stacks 21 of the first block 11 in H₂ are shown, partially and schematically, in figures 3 and 4; while they have been added by way of example in the general configuration of figure 1, also these variations may be applied to both general layouts of figures 1 and 2.

In the variation of figure 3, separator 27 is configured so as to separate from the anode exhaust exiting from anodes 25 of stacks 21 of the first block 11 a stream of H₂O and, separately, a stream substantially of pure H₂; this stream of "pure" H₂ is recirculated to the same anodes 25 through the anode recirculation line 51; the residual stream of separator 27, containing CO₂, H₂, residual fuels, H₂S, etcetera, is conveyed via a treating line 62 to burner 13 (or another burner), where residual fuels, remained with the CO₂ to be sent to capture, are eliminated by combustion in O₂ or in mixtures O₂/CO₂, and then to another final separator 63 of CO₂.

In the example of figure 3, also stack 22 of the second block 12 includes MCFC cells with indirect internal reformer, with recirculation of the stream rich

in H₂ exiting from separator 28 on anodes 26.

In the variation of figure 4, the system comprises a further auxiliary separator 64 arranged between the outlet of reformer 14 and anodes 25 of stack 21 of the first block 11 and thus along the anode inlet line 41. The auxiliary separator 64 removes CO₂ and H₂O from the stream supplied to anodes 25.

The invention also allows a wide freedom of selection as regards the type of stacks to be used for the different blocks.

Using stacks with indirect internal reformer IIR or without internal reformer for the first block and stacks with internal reformer (either direct DIR or indirect IIR) for the second block (and any following ones) is the preferable choice in most cases, where it is convenient to work at atmospheric pressure. But also different combinations may conveniently be used in special situations. The use of cells with DIR reformer in the first block may also be contemplated, where while it removes CO₂, it mainly plays the role of reducing the NO_x to the benefit of the following blocks, in the case of sulfur-free flue gas.

Finally, it is understood that further changes and variations may be made to the system and method described and shown herein without departing from the scope of the appended claims.

CLAIMS

1. A multi-stack MCFC system (1) for separating CO₂ from combustion flue gas containing SO_x and NO_x, comprising a first MCFC-CCS block (11) of MCFC stacks and at least one second MCFC-CCS block (12) of MCFC stacks, at least one burner (13), and a connection system (15) that connects the blocks (11, 12) and the burner (13); the blocks (11, 12) comprising respective stacks (21, 22) of MCFC cells, having respective cathodes (23, 24) and anodes (25, 26), and respective separators (27, 28) acting on the anodic exhausts of the stacks (21, 22); the system being characterized in that the connecting system (15) is configured so as:

- the cathodes (23, 24) of the stacks (21, 22) of the two blocks (11, 12) are connected in series;

- the flue gas to treat enters only into the cathodes (23) of the stacks (21) of the first block (11), with or without addition of air; the second block (12), and possible following blocks, are only supplied with flue gas that has already passed through the cathodes (23) of stacks (21) of the first block (11);

- the anodes (25, 26) of the stacks (21, 22) of each block (11, 12) are connected to respective separators (27, 28), that remove H₂O and separate a stream containing CO₂ for the capture from a stream rich in H₂;

- the separators (27, 28) and the lines that manipulate the anodic exhaust are organized in such a way that H₂S and N₂ are expelled from the system.

2. A system according to claim 1, wherein the
5 burner (13) is associated to a reformer (14).

3. A system according to claim 1 or 2, wherein the separators (27, 28) are organized so as to process the anodic exhaust of the stacks (21) of the first block (11) by removing H₂O, extracting CO₂ and also removing
10 H₂S, up to obtain a H₂S residue below a predetermined value; and so as at least one portion of the stream rich in H₂ exiting from the separator (27) connected to the anodic exits of the stacks (21) of the first block (11) is conveyed, directly or after passing through the
15 anodes (26) of stacks (22) of one or more other blocks (12), to the burner (13), or to another external burner, or to an external user so as to avoid build-up phenomenon of N₂.

4. A system according to claim 3, wherein the
20 stream rich in H₂ and containing residual fuels exiting from the separator (27) of the first block (11) is conveyed: to the anodes (26) of stacks (22) of the second block (12), via an anodic line (44), either directly or by passing through a reformer (32)
25 associated to said stacks (22) of the second block (12); and/or to the plant hosting the system (1), via an

anodic exit line (45), to be consumed herein; and/or to the anodes (25) of the stacks (21) of the first block (11), via an anodic recirculation line (51) that joins with an anode inlet line (41); and/or to the burner
5 (13), via a further recirculation line (52) that joins with a recirculation line (47) coming, after passing through the separator (28) of the second block (12), from the anodes (26) of the second block (12).

5. A system according to claim 3 or 4, wherein
10 the stream rich in H₂ and containing residual fuels exiting from the separator (28) of the second block (12) is conveyed: via a recirculation line (47) to the burner (13), where the residual fuels contained in said stream are burned and the heat generated is recovered for
15 sustaining reactions in the reformer (14) associated to the burner (13) and for heating the oxidizing gas containing the flue gas supplied to the first block (11); and/or to the anodes (25) of the stacks (21) of the first block (11), via an auxiliary line (53) that
20 departs from the recirculation line (47) and joins with the anode inlet line (41), before going to the burner (13) or to another burner, inside or outside the blocks (11, 12), or to an external user.

6. A system according to one of claims 3 to 5,
25 having a flue gas inlet (33) that is arranged upstream of the burner (13) and is connected to the burner (13)

via a flue gas supply line (34), through which the flue gas enters into the burner (13); and the burner (13) has an exit connected to the cathodes (23) of the stacks (21) of the first block (11), via a cathode inlet line
5 (36).

7. A system according to one of claims 3 to 5, wherein the flue gas is supplied to the cathodes (23) of the stacks (21) of the first block (11) via a flue gas supply line (34) that connects a flue gas inlet (33) to
10 the cathodes (23) of the first block (11); and the system (1) comprises a MCFC supplementary group (55), formed by one or more stacks (56) of MCFC cells having respective cathodes (57) and anodes (58); the burner (13) having an exit connected to the cathodes (57) of
15 the supplementary group (55), so as the gas stream exiting from the burner (13) supplies said cathodes (57) of the supplementary group (55).

8. A system according to claim 7, wherein the supplementary group (55) has an anodic exit connected,
20 via an anodic line (60), to a separator (59) that removes H₂O and CO₂ from a residual stream containing H₂.

9. A system according to claim 7 or 8, wherein a fuel supply line (42) supplies, as well as the reformer
25 (14) associated to the burner (13), also the anodes (58) of the supplementary group (55).

10. A system according to one of the preceding claims, wherein the separator (27) of the first block is configured so as to separate from the anodic exhaust exiting from the anodes (25) of the stacks (21) of the first block (11) a stream of H₂O and, separately, a stream substantially of pure H₂ that is recirculated to the same anodes (25) of the first block (11); the residual stream of the separator (27) of the first block (11) being conveyed via a treating line (62) to the burner (13), where residual fuels, remained with the CO₂ to be sent to capture, are eliminated by combustion in O₂ or in mixtures O₂/CO₂, and then to another final separator (63) of CO₂.

11. A system according to one of the preceding claims, comprising a further auxiliary separator (64) arranged between the exit of the reformer (14) associated to the burner (13) and the anodes (25) of the stacks (21) of the first block (11), along an anode inlet line (41); said auxiliary separator (64) being configured for removing CO₂ and H₂O from the stream supplied to the anodes (25) of the first block (11).

12. A method for separating CO₂ from combustion flue gas containing SO_x and NO_x by means of a multi-stack MCFC system (1), comprising the steps of:

- providing a multi-stack MCFC system (1) comprising a first MCFC-CCS block (11) of MCFC stacks

and at least one second MCFC-CCS block (12) of MCFC stacks; the blocks (11, 12) comprising respective stacks (21, 22) of MCFC cells, having respective cathodes (23, 24) and anodes (25, 26), and respective separators (27, 28) acting on the anodic exhausts of the stacks (21, 22); the cathodes (23, 24) of the stacks (21, 22) of the two blocks (11, 12) being connected in series;

- supplying the flue gas to treat only to the cathodes (23) of the stacks (21) of the first block (11), with or without addition of air; while the second block (12), and possible following blocks, are only supplied with flue gas that has already passed through the cathodes (23) of stacks (21) of the first block (11);

- processing the anodic exhaust of the anodes (25, 26) of the stacks (21, 22) of each block (11, 12) with respective separators (27, 28) for removing H₂O and separating a stream containing CO₂ for the capture from a stream rich in H₂, and so as to expel H₂S and N₂ from the system (1).

13. A method according to claim 12, comprising the step of processing the anodic exhaust of the stacks (21) of the first block (11) by removing H₂O, extracting CO₂ and also removing H₂S, up to obtain a H₂S residue below a predetermined value; and so as at least one portion of the stream rich in H₂ exiting from the separator (27)

connected to the anodic exits of the stacks (21) of the first block (11) is conveyed, directly or after passing through the anodes (26) of stacks (22) of one or more other blocks (12), to the burner (13), or to another
5 external burner, or to an external user, so as to avoid build-up phenomenon of N₂.

14. A method according to claim 13, wherein the stream rich in H₂ and containing residual fuels exiting from the separator (27) of the first block (11) is
10 conveyed: to the anodes (26) of stacks (22) of the second block (12), via an anodic line (44), either directly or by passing through a reformer (32) associated to said stacks (22) of the second block (12); and/or to the plant hosting the system (1), via an
15 anodic exit line (45), to be consumed herein; and/or to the anodes (25) of the stacks (21) of the first block (11), via an anodic recirculation line (51) that joins with an anode inlet line (41); and/or to the burner (13), via a further recirculation line (52) that joins
20 with a recirculation line (47) coming, after passing through the separator (28) of the second block (12), from the anodes (26) of the second block (12).

15. A method according to claim 13 or 14, wherein the stream rich in H₂ and containing residual fuels
25 exiting from the separator (28) of the second block (12) is conveyed: via a recirculation line (47) to the burner

(13), where the residual fuels contained in said stream are burned and the heat generated is recovered for sustaining reactions in the reformer (14) associated to the burner (13) and for heating the oxidizing gas containing the flue gas supplied to the first block (11); and/or to the anodes (25) of the stacks (21) of the first block (11), via an auxiliary line (53) that departs from the recirculation line (47) and joins with the anode inlet line (41), before going to the burner (13) or to another burner, inside or outside the blocks (11, 12), or to an external user.

16. A method according to one of claims 13 to 15, wherein the flue gas are supplied to the burner (13) and are then conveyed to the cathodes (23) of the stacks (21) of the first block (11).

17. A method according to one of claims 13 to 15, wherein the flue gas are supplied to the cathodes (23) of the stacks (21) of the first block (11); and the method comprises the step of conveying the gas stream exiting from the burner (13) to the cathodes (57) of a supplementary MCFC group (55), formed by one or more stacks (56) of MCFC cells having respective cathodes (57) and anodes (58).

18. A method according to claim 17, comprising the step of conveying the stream exiting from the anodes (58) of the supplementary group (55) to a separator (59)

that removes H₂O and CO₂ from a residual stream containing H₂.

19. A method according to one of claims 12 to 18, comprising the step of separating from the anodic exhaust exiting from the anodes (25) of the stacks (21) of the first block (11) a stream of H₂O and, separately, a stream of substantially only H₂ that is recirculated to the same anodes (25) of the first block (11), and obtaining a residual stream, containing residual fuels, that is conveyed to the burner (13), where said residual fuels, remained with the CO₂ to be sent to capture, are eliminated by combustion in O₂ or in mixtures O₂/CO₂, and then to a final CO₂ separation step.

20. A method according to one of claims 12 to 19, comprising a step of removing CO₂ and H₂O from the stream supplied to the anodes (25) of the first block (11).

21. A method according to one of claims 12 to 20, comprising the step of passing through the anodes (25) of the stacks (21) of the first block (11), in form of H₂, at least one portion of the fuel needed by the second block (12) and/or by possible other blocks of stacks, by the hosting plant and/or by other users.

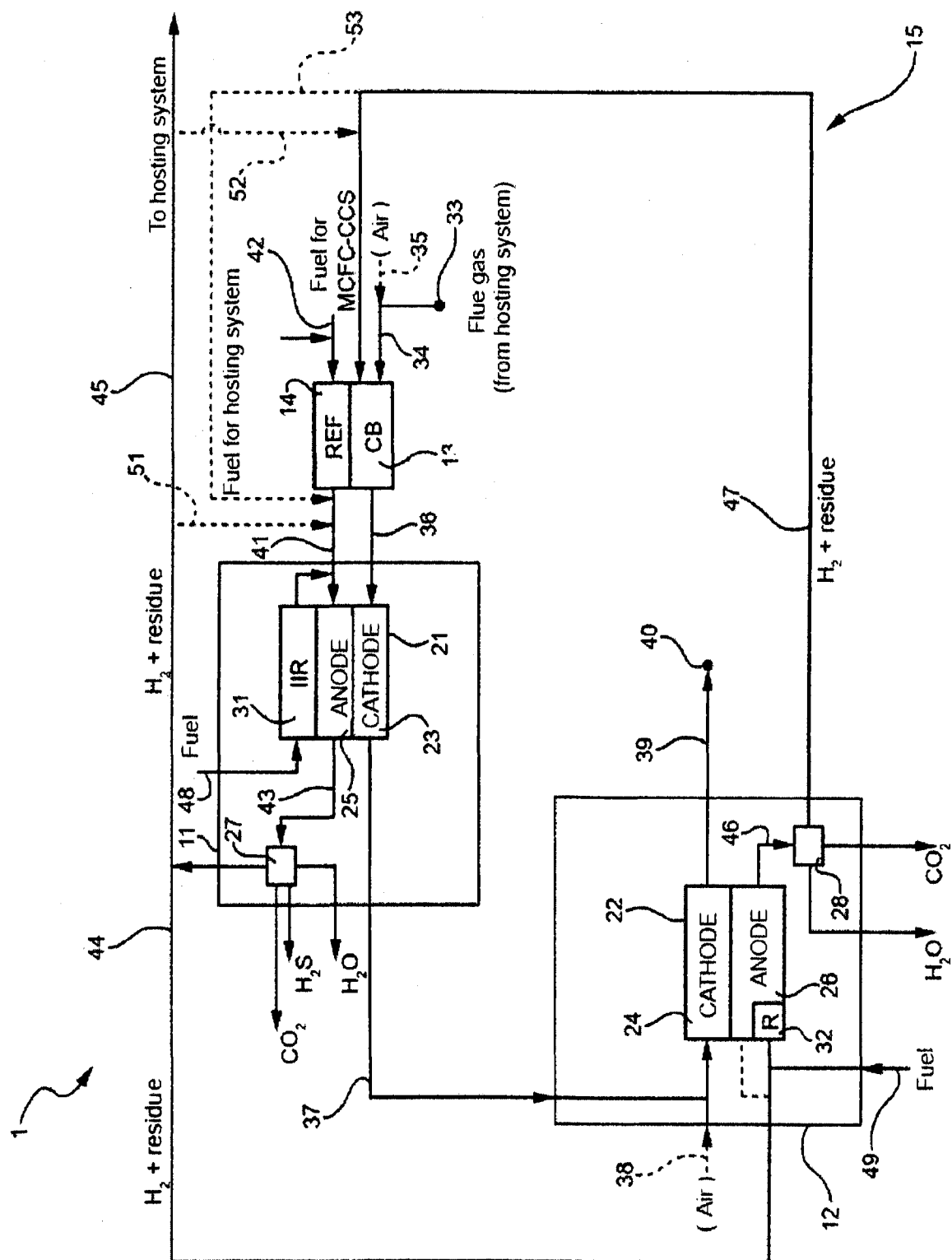


FIG. 1

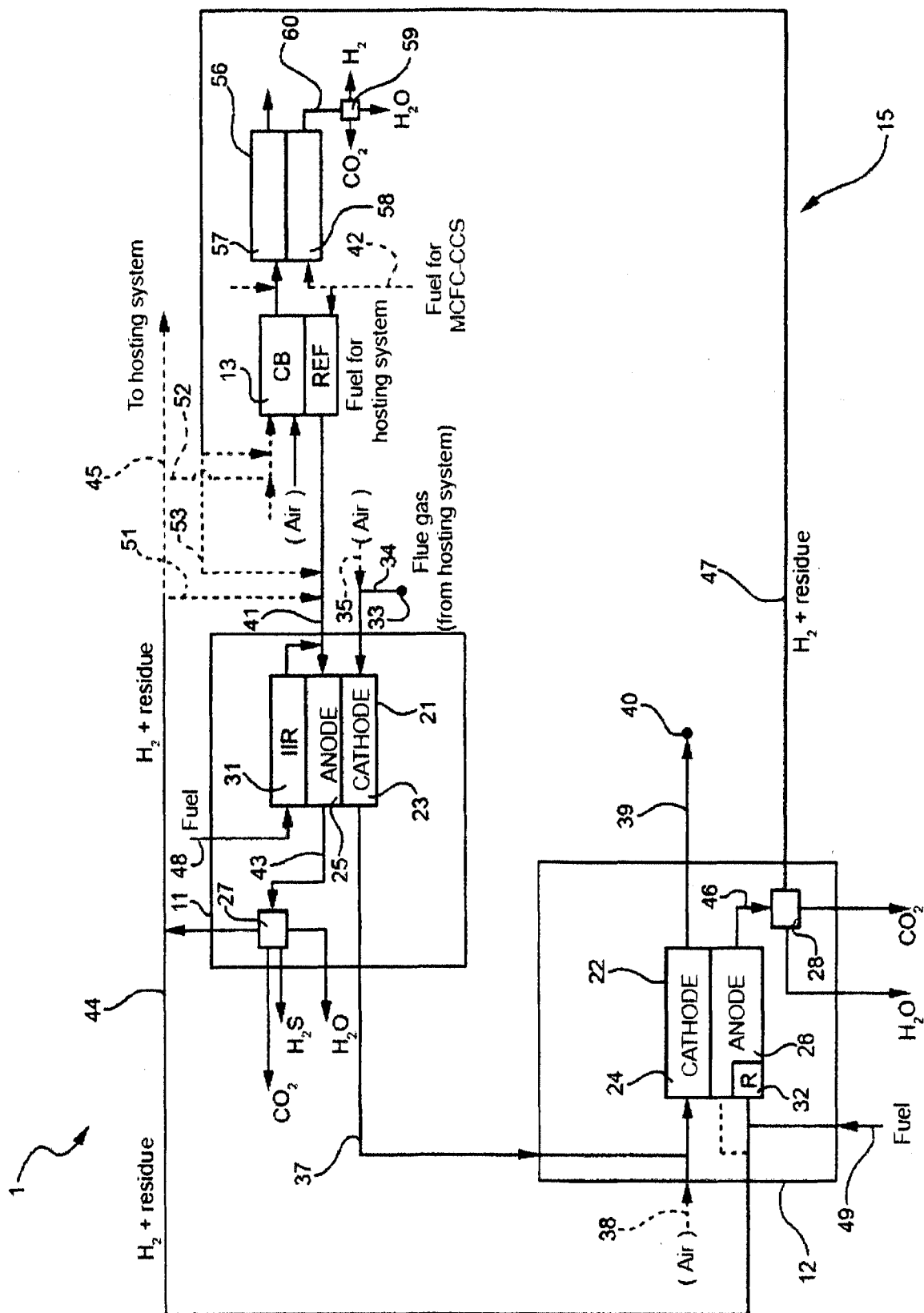


FIG. 2

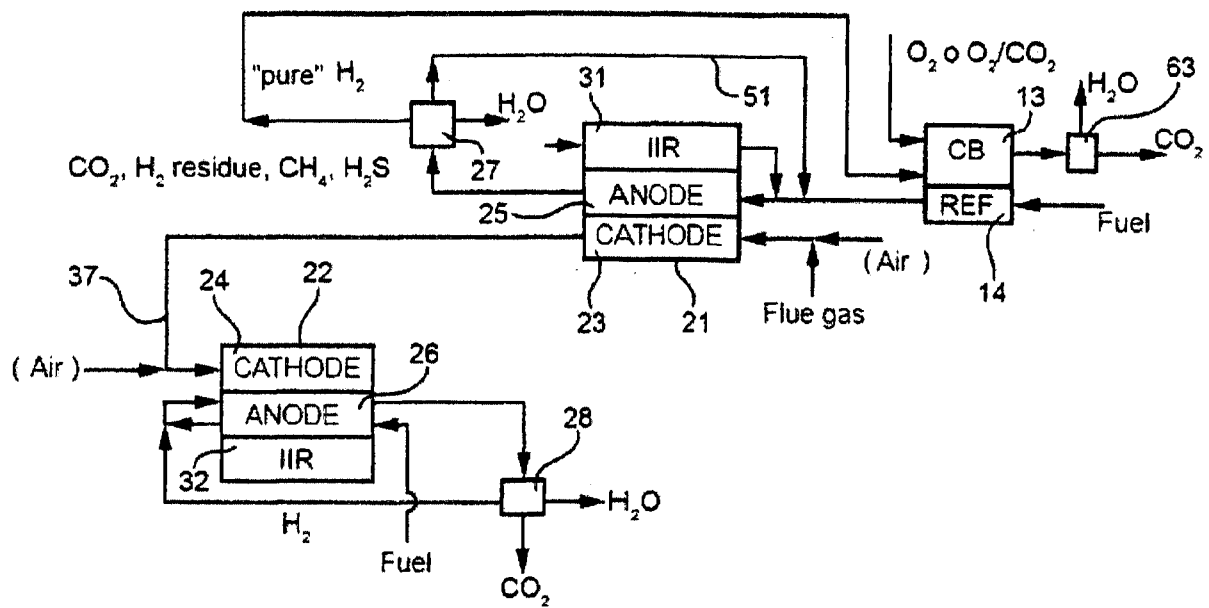


FIG. 3

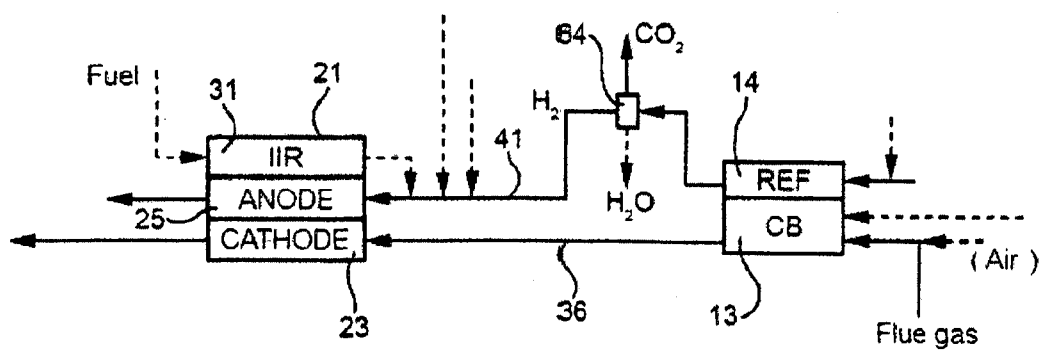


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2012/053197

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01M8/04 H01M8/14 H01M8/06
ADD.

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 practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE EPODOC	12
Y	EUROPEAN PATENT OFFICE, THE HAGUE, NL; 2009, XP002668940, abstract	
L	& IT MI20 092 259 A1 (ANSALDO FUEL CELLS S P A) 22 June 2011 (2011-06-22) -& WO 2011/077224 A1 (ANSALDO FUEL CELLS S P A [IT]; CAPRILE LUCIANO [IT]; PASSALACQUA BIAGI) 30 June 2011 (2011-06-30) figure 1 page 12, line 4 - page 13, line 11 ----- -/-	1-6,11, 13-16, 20,21



Further documents are listed in the continuation of Box C.



See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

23 August 2012

Date of mailing of the international search report

30/08/2012

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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2012/053197

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2010/125443 A1 (ANSALDO FUEL CELLS S P A [IT]; CAPRILE LUCIANO [IT]; PASSALACQUA BIAGI) 4 November 2010 (2010-11-04) page 4, line 19 - page 5, line 6 page 7, line 23 - page 10, line 9 page 12, line 22 - page 13, line 1 page 13, line 29 - page 14, line 14 -----	1-6,11, 13-16, 20,21
A	US 2005/271914 A1 (FAROOQUE MOHAMMAD [US] ET AL) 8 December 2005 (2005-12-08) figures 1-3 abstract examples 1, 2 -----	1-21

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2012/053197

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WO 2010125443	A1	04-11-2010	NONE

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			EP 1790027 A2 30-05-2007
			JP 2008507113 A 06-03-2008
			KR 20070057131 A 04-06-2007
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			WO 2007015689 A2 08-02-2007
