A method of reducing carbon monoxide from a hydrocarbon reformate includes sequentially channeling an initial amount of reformate into a plurality of reactors comprising a bifunctional material. The carbon monoxide is preferentially chemisorbed by the bifunctional material such that a chemisorption capacity of the bifunctional material is reduced. An additional amount of the reformate is sequentially restricted into the reactors. A heated oxygen containing gas is sequentially passed through the reactors to convert the carbon monoxide to carbon dioxide. Thereby, the chemisorption capacity of the bifunctional material in the reactors is sequentially regenerated.
## FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

<table>
<thead>
<tr>
<th>AL</th>
<th>Albania</th>
<th>ES</th>
<th>Spain</th>
<th>LS</th>
<th>Lesotho</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM</td>
<td>Armenia</td>
<td>FI</td>
<td>Finland</td>
<td>LT</td>
<td>Lithuania</td>
</tr>
<tr>
<td>AT</td>
<td>Austria</td>
<td>FR</td>
<td>France</td>
<td>LU</td>
<td>Luxembourg</td>
</tr>
<tr>
<td>AU</td>
<td>Australia</td>
<td>GA</td>
<td>Gabon</td>
<td>LV</td>
<td>Latvia</td>
</tr>
<tr>
<td>AZ</td>
<td>Azerbaijan</td>
<td>GB</td>
<td>United Kingdom</td>
<td>MC</td>
<td>Monaco</td>
</tr>
<tr>
<td>BA</td>
<td>Bosnia and Herzegovina</td>
<td>GE</td>
<td>Georgia</td>
<td>MD</td>
<td>Republic of Moldova</td>
</tr>
<tr>
<td>BB</td>
<td>Barbados</td>
<td>GH</td>
<td>Ghana</td>
<td>MG</td>
<td>Madagascar</td>
</tr>
<tr>
<td>BE</td>
<td>Belgium</td>
<td>GN</td>
<td>Guinea</td>
<td>MK</td>
<td>The former Yugoslavia</td>
</tr>
<tr>
<td>BF</td>
<td>Burkina Faso</td>
<td>GR</td>
<td>Greece</td>
<td>ML</td>
<td>Mali</td>
</tr>
<tr>
<td>BG</td>
<td>Bulgaria</td>
<td>HU</td>
<td>Hungary</td>
<td>MN</td>
<td>Mongolia</td>
</tr>
<tr>
<td>BJ</td>
<td>Benin</td>
<td>IE</td>
<td>Ireland</td>
<td>MR</td>
<td>Mauritania</td>
</tr>
<tr>
<td>BR</td>
<td>Brazil</td>
<td>IL</td>
<td>Israel</td>
<td>MW</td>
<td>Malawi</td>
</tr>
<tr>
<td>BY</td>
<td>Belarus</td>
<td>IS</td>
<td>Ireland</td>
<td>MX</td>
<td>Mexico</td>
</tr>
<tr>
<td>CA</td>
<td>Canada</td>
<td>IT</td>
<td>Italy</td>
<td>NE</td>
<td>Niger</td>
</tr>
<tr>
<td>CF</td>
<td>Central African Republic</td>
<td>JP</td>
<td>Japan</td>
<td>NL</td>
<td>Netherlands</td>
</tr>
<tr>
<td>CG</td>
<td>Congo</td>
<td>KE</td>
<td>Kenya</td>
<td>NO</td>
<td>Norway</td>
</tr>
<tr>
<td>CH</td>
<td>Switzerland</td>
<td>KG</td>
<td>Kyrgyzstan</td>
<td>NZ</td>
<td>New Zealand</td>
</tr>
<tr>
<td>CI</td>
<td>Côte d'Ivoire</td>
<td>KP</td>
<td>Democratic People's Republic of Korea</td>
<td>PL</td>
<td>Poland</td>
</tr>
<tr>
<td>CM</td>
<td>Cameroon</td>
<td>KR</td>
<td>Republic of Korea</td>
<td>PT</td>
<td>Portugal</td>
</tr>
<tr>
<td>CN</td>
<td>China</td>
<td>KZ</td>
<td>Kazakhstan</td>
<td>RO</td>
<td>Romania</td>
</tr>
<tr>
<td>CU</td>
<td>Cuba</td>
<td>LC</td>
<td>Saint Lucia</td>
<td>RU</td>
<td>Russian Federation</td>
</tr>
<tr>
<td>CZ</td>
<td>Czech Republic</td>
<td>LI</td>
<td>Liechtenstein</td>
<td>SD</td>
<td>Sudan</td>
</tr>
<tr>
<td>DE</td>
<td>Germany</td>
<td>LK</td>
<td>Sri Lanka</td>
<td>SE</td>
<td>Sweden</td>
</tr>
<tr>
<td>DK</td>
<td>Denmark</td>
<td>LR</td>
<td>Liberia</td>
<td>SG</td>
<td>Singapore</td>
</tr>
<tr>
<td>EE</td>
<td>Estonia</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SI</td>
<td>Slovenia</td>
<td>SK</td>
<td>Slovakia</td>
<td>SN</td>
<td>Senegal</td>
</tr>
<tr>
<td>SZ</td>
<td>Swaziland</td>
<td>TD</td>
<td>Chad</td>
<td>TG</td>
<td>Togo</td>
</tr>
<tr>
<td>TJ</td>
<td>Tajikistan</td>
<td>TM</td>
<td>Turkmenistan</td>
<td>TR</td>
<td>Turkey</td>
</tr>
<tr>
<td>TT</td>
<td>Trinidad and Tobago</td>
<td>UA</td>
<td>Ukraine</td>
<td>UG</td>
<td>Uganda</td>
</tr>
<tr>
<td>US</td>
<td>United States of America</td>
<td>UZ</td>
<td>Uzbekistan</td>
<td>VN</td>
<td>Viet Nam</td>
</tr>
<tr>
<td>YU</td>
<td>Yugoslavia</td>
<td>ZW</td>
<td>Zimbabwe</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional application no. 60/100,966 filed September 18, 1998.

BACKGROUND OF THE INVENTION

This invention relates to an apparatus and method for removing carbon monoxide from a hydrocarbon reformate used in fuel cell applications. More specifically, it relates to the use of multiple beds comprising a bifunctional material to preferentially adsorb carbon monoxide from a stream of reformate, and the use of a pre-heated oxidizing sweep gas to oxidize the accumulated carbon monoxide, thereby regenerating the bifunctional material.

The internal combustion engine found in most cars and trucks burns a hydrocarbon fuel such as diesel or gasoline to drive pistons or rotary mechanisms by the force of the expanding gas. Many electrical power plants burn fossil fuel to produce electrical energy through combustion turbines. These processes suffer from a number of limitations. They are inefficient because of the intrinsic limit of the thermodynamic principles involved. Burning of fossil fuel is oftentimes incomplete and produces harmful byproducts such as carbon monoxide, nitrogen oxides and various hydrocarbons in the emissions, which have resulted in environmental pollution. In addition, there is a growing awareness that we are rapidly depleting the non-renewable energy resources on this planet. This, in turn, has led to concerns about the reduction of energy consumption by increasing fuel efficiency.
Fuel cells convert the chemical energy in the fuel directly into electrical energy through an electro-chemical reaction. Because they do not operate on the principle of gas expansion through combustion, they do not suffer the same limitations of thermodynamic efficiency commonly found in automobile engines and steam turbines. Accordingly, it is possible for fuel cells to achieve a level of efficiency far greater than that seen in most traditional industrial processes. Additionally, fuel cells make it possible for fuel processors to use renewable forms of energy such as methanol and ethanol, thereby conserving the limited fossil fuel resources of the planet. Moreover, because of the operating environment of a fuel processor and fuel cell, hydrocarbons, nitrogen oxides and carbon monoxide emissions are negligible, approaching a zero emission state.

While there are several types of fuel cells existing in practice, this invention is targeted mainly for applications in polymer electrolyte fuel cells (PEFCs) which are also known as proton exchange membrane fuel cells (PEMFCs). A very efficient PEFC uses pure hydrogen for fuel and oxygen for an oxidant. Pure hydrogen, however, has traditionally been difficult to handle and relatively expensive to store and distribute. Consequently, attempts have been made to use hydrogen rich gas mixtures obtained from reforming of various hydrocarbon fuels. To obtain a convenient and safe source of hydrogen for the fuel cells, on-board reforming of hydrocarbon based fuels, such as gasoline and methanol, is expected to be utilized. These reformed fuels, or reformate, usually contain hydrogen, nitrogen, carbon dioxide, and low levels of carbon monoxide in the range from 100's of ppm to a few percent. While the presence of carbon dioxide generally has little effect on the operation efficiency of a fuel cell, even relatively low concentrations of carbon monoxide can degrade fuel cell performance. The degradation results from the carbon monoxide chemically adsorbing over the active sites in the electrode of the fuel cell. Thus, the removal of carbon monoxide from fuel has become a major concern in the advancement of PEFC technology.
Attempts at carbon monoxide removal have been disclosed in numerous patents. One method for removing carbon monoxide from a hydrocarbon reformate is known as the pressure swing method disclosed in Nishida et al., U.S. Patent no. 4,743,276 and Golden et al., U.S. Patent no. 5,531,809. Because the adsorption of carbon monoxide is pressure sensitive in many substances, by alternately raising and lowering the pressure within the adsorption chamber, carbon monoxide can be alternately adsorbed and purged from the adsorbent substance. There are, however, multiple drawbacks to the pressure swing absorption method, including the need for bulky and expensive pressure resistant tanks, as well as pressure and/or vacuum pump apparatus which are necessary to cycle the pressure. The parasitic weight and volume of these devices make it difficult to apply the pressure swing adsorption method for transportation applications such as a fuel cell power plant for an automobile. A second disadvantage of this approach is the significant power expenditure necessary to cycle the pressurization and depressurization steps. This additional power consumption will result in the reduction of overall efficiency of the fuel cell system. Yet another disadvantage of this process is that the toxic carbon monoxide released from desorption has to be converted to carbon dioxide with additional process steps and equipment.

Another prior art process for removing carbon monoxide involves membrane separation, whereby the hydrogen in the reformate can be separated by a metallic membrane. For example, R. E. Buxbaum, U.S. Patent no. 5,215,729 discloses a palladium based metallic membrane which provides the selectivity for hydrogen separation up to 100%. Therefore, it could remove carbon monoxide and other components from hydrogen which is the fuel for the PEFC. Although highly selective, the process has several disadvantages. Since it uses precious metal as membrane material, it is expensive. Furthermore, the reformate has to be pressurized to facilitate the separation process which results in parasitic power loss and equipment complexity.
Yet another method has been referred to as preferential carbon monoxide oxidation (PROX), as described for example in Vanderborgh et al., in U. S. Patent no. 5,271,916; Pow et al., U.S. Patent no. 5,316,747; and Aoyama, U.S. Patent no. 5,843,195. This process involves the preferential oxidation of carbon monoxide in the presence of hydrogen by injecting air or an oxygen containing gas into a reformate stream. The chemical reaction combines carbon monoxide and oxygen to form carbon dioxide, thereby eliminating the carbon monoxide present in the reformate. A significant limitation of the PROX method disclosed in the above patents, however, is the parasitic consumption of hydrogen. When an oxidant is introduced into a stream of reformate in a PROX device, the oxidant concentration has to be stoichiometrically higher than the amount of CO in order to reduce the carbon monoxide concentration to the acceptable level. The excess oxidant reacts with hydrogen; therefore, it is impossible to avoid parasitic consumption of hydrogen in the process. This problem is addressed in part by Buswell et al., U.S. Patent nos. 5,518,705 and 5,750,076, and Meltser et al, U.S. Patent no. 5,637,415 whereby the flow rate of oxidant being introduced into a reformate stream is limited. By limiting the amount of oxygen introduced, the parasitic consumption of hydrogen can be reduced.

In addition to the problem of the parasitic consumption of hydrogen by the oxidizing agent, another potential shortcoming of the PROX is known as the "reverse shift" arising from the presence of carbon dioxide. This occurs when carbon dioxide reacts with hydrogen to form carbon monoxide and water. Because the "reverse shift" is temperature dependent, it is difficult to reduce carbon monoxide levels below a certain level when the temperature exceeds an upper threshold. Trocciola et al., U.S. Patent no. 5,330,727, disclose a two step process to avoid the reverse shift effect. The first step involves mixing an oxidant (typically air) with the fuel, and heating it to about 320 degrees F and exposing the fuel/air mixture to a material such as platinum. The high temperature is required since the efficient oxidation of carbon monoxide cannot take place at lower temperatures in the presence of
high levels of carbon monoxide. Once the carbon monoxide levels are reduced to about 60 ppm, the second step involves the more efficient oxidation at lower temperatures, where the reverse shift does not occur. Therefore, Trocciola et al. allow the carbon dioxide to remain mixed with the reformate. Vanderborgh et al., U.S. Patent no. 5,271,916 disclose a similar multi-step process.

Although temperature control may reduce or eliminate the "reverse shift" effect, it does not resolve the problem of parasitic consumption of hydrogen when an oxidant is mixed with a reformate to oxidize carbon monoxide. Furthermore, another significant limitation of PROX is its poor tolerance towards the variation of CO input level in the reformate. To minimize the parasitic hydrogen loss, the oxygen to CO ratio has to be kept at a relatively low level. Yet, the CO input level often varies as the result of change of the fuel cell power output, thus the reformate throughput. It is difficult to constantly match the CO input level with the oxygen level in a dynamic environment. Consequently, unreacted CO will leak through PROX reactor, impacting fuel cell performance downstream.

Bellows et al., U.S. Patent no. 5,604,047 disclose a process whereby a stream of hydrocarbon reformate is channeled across a bed containing an adsorbent that preferentially adsorbs carbon monoxide. Before the adsorbent has become saturated with carbon monoxide, a regeneration phase begins. Regeneration involves removing the adsorbed CO from the adsorbent preferably using a non-oxidizing sweep gas, although an oxidizing sweeping gas can be used. In either event, no discussion is apparently provided about whether the sweep gas should or must be pre-heated before it enters the bed and/or how pre-heating can effect performance. In the regeneration phase, the bed is isolated from the fuel supply, thereby avoiding parasitic consumption of hydrogen. With the preferred sweep gas being steam that is channeled through the bed, carbon monoxide can be subsequently removed through desorption. The desorbed carbon monoxide in the steam can either be further oxidized through an additional step or be recycled back to a
fuel processor. After regeneration of the absorbent, the sweep gas is turned off and fuel is again channeled across the bed.

Disadvantages, however, remain in this process. With the preferred use of steam, oxidation of carbon monoxide outside of the bed requires additional processing and apparatus. Also, two beds alternately remove carbon monoxide from reformate and regenerate. Because both beds actively transition at the same time, there is a potential momentary lapse in fuel flow. Additionally, one bed must be “off line” (i.e., not removing carbon monoxide) for the entire time the other bed is “on line.” This results in an inefficiency wherein a regenerated bed is unavailable for carbon monoxide removal until the other bed is taken off line. Furthermore, using steam to sweep CO from the adsorbent requires a relatively high amount of energy due to a large latent heat of water vaporization. Therefore, the process will reduce the overall efficiency.

Other disclosures related to carbon monoxide removal are found in Frost et al., U.S. Patent no. 5,871,860; Guro et al., U.S. Patent no. 5,073,356; Golden et al., U.S. Patent no. 5,126,310; Peng, U.S. Patent no. 5,529,763; and Kawatsu, U.S. Patent no. 5,712,052.

As can be seen, there is a need for an improved method of and apparatus for removing carbon monoxide from a hydrocarbon reformate and regenerating a catalytic material that reduces or eliminates both parasitic consumption of hydrogen and the “reverse shift” effect. Also needed is a method and apparatus that optimizes the speed, robustness and thoroughness of the regeneration of CO removal capacity and optimizes the oxidation of carbon monoxide. An apparatus and method is needed that minimizes the amount of time a bed is “off line” as a result of the regeneration phase, displays enhanced tolerance to carbon monoxide concentration swings, can be operated simply and economically, and can operate at the temperature and pressures similar to that of a fuel cell.
SUMMARY OF THE INVENTION

In the present invention, a method of reducing carbon monoxide from a hydrocarbon reformate comprises the steps of moving an initial amount of reformate through a bed comprising a bifunctional material that preferentially adsorbs carbon monoxide over hydrogen; preferentially adsorbing the carbon monoxide by means of the bifunctional material such that an adsorption capacity of the bifunctional material is reduced; restricting an additional amount of reformate from moving through the bed; and passing a pre-heated oxygen containing gas through the bed; and converting the carbon monoxide to carbon dioxide, thereby regenerating the adsorption capacity of the bifunctional material. A bifunctional material in this invention is defined as a material that has both the capability of selectively adsorbing carbon monoxide as well as the capability of catalytically oxidizing CO in the presence of an oxidizing gas.

In another aspect of the present invention, a method of reducing carbon monoxide from a hydrocarbon reformate comprises the steps of sequentially channeling an initial amount of reformate into a plurality of plug-flow reactors comprising a bifunctional material that preferentially chemisorbs carbon monoxide; preferentially chemisorbing the carbon monoxide by the bifunctional material such that a chemisorption capacity of the bifunctional material is reduced; sequentially restricting an additional amount of the reformate into the plug-flow reactors; passing a pre-heated oxygen containing gas sequentially through the plug-flow reactors; and converting the carbon monoxide to carbon dioxide, thereby sequentially regenerating the chemisorption capacity of the bifunctional material in the plug-flow reactors.

The present invention also provides a method of providing D.C. power from a hydrocarbon reformate containing carbon monoxide, comprising the steps of processing a hydrocarbon fuel in a fuel processor to form a carbon monoxide-containing hydrocarbon reformate; sequentially channeling the reformate into a plurality of plug-flow reactors individually comprising a
bifunctional material that preferentially adsorbs carbon monoxide; sequentially adsorbing the carbon monoxide by the plug flow reactors; passing a pre-heated oxygen-containing gas sequentially through the plug-flow reactors; sequentially catalyzing the carbon monoxide adsorbed on the bifunctional material to carbon dioxide, thereby regenerating the adsorption capacity of the plug flow reactors; producing a substantially carbon monoxide free reformate from the plug flow reactors; and passing the carbon monoxide-free reformate into a fuel cell to produce D.C. power;.

In another aspect of the present invention, a system for removing carbon monoxide from a hydrocarbon reformate comprises a first bed comprising a first bifunctional material that preferentially adsorbs carbon monoxide from the reformate; a second bed comprising a second bifunctional material that preferentially adsorbs carbon monoxide from the reformate; a first valve operatively connecting the first and second beds, the first valve for sequentially channeling the reformate and a pre-heated oxygen containing sweep gas between the first and second beds; a heater for pre-heating the oxygen containing sweep gas; and a second valve operatively connecting the first and second beds, the second valve for sequentially channeling a substantially carbon monoxide free reformate from the first and second beds.

In still another embodiment, the present invention provides a fuel processor that processes a hydrocarbon fuel containing carbon monoxide; an adsorption and catalytic bed downstream of the fuel processor, the bed comprising a bifunctional material having one or multiple active components and a support, the bifunctional material being capable of adsorbing carbon monoxide preferentially over hydrogen in the hydrocarbon fuel and capable of catalyzing a reaction between the carbon monoxide and an oxygen containing sweep gas; and a heating element for heating the sweep gas.

These and other features, aspects and advantages of the present invention will become better understood with reference to the following drawings, description and claims.
BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a block diagram of a method and apparatus for removing carbon monoxide from a fuel according to an embodiment of the present invention;

Figure 2a is a schematic view of a multiple bed configuration of an adsorption-catalytic oxidation (ACO) system according to an embodiment of the present invention;

Figure 2b is a plan view of an ACO system with a rotating bed configuration according to an embodiment of the present invention;

Figure 2c is a side view of the ACO system depicted in Figure 2b;

Figure 2d is a perspective view of the ACO system depicted in Figure 2c;

Figure 3 is a side view of a plug-flow reactor that can be used in the ACO system of Figures 2a-d;

Figure 4 depicts a bifunctional material in an adsorption-catalytic oxidation (ACO) processor according to an embodiment of the present invention;

Figure 5 is a graph of a carbon monoxide concentration versus time wherein 123 ppm carbon monoxide was channeled into a 10cc ACO bed comprising a catalyst of 6 wt. % Pt over Al₂O₃ according to an embodiment of the present invention;

Figure 6 is a graph of a carbon monoxide concentration versus time wherein 123 ppm carbon monoxide was channeled into a 10cc bed comprising a catalyst of 7 wt. % Pd over Al₂O₃ according to an embodiment of the present invention;

Figure 7 is a graph of carbon monoxide concentration versus time wherein 1500 ppm CO was channeled into a 7 cc bed comprising a catalyst of 4wt.% Ru over alumina according to an embodiment of the present invention.
DETAILED DESCRIPTION OF THE INVENTION

Figure 1 is a block diagram of a method and system 10 for removing carbon monoxide from a fuel used for a PEFC stack according to one embodiment of the present invention. A hydrocarbon fuel 26 is processed by a fuel processor 27 into a hydrocarbon reformate 28 comprising hydrogen needed for fuel cell operation, as well as carbon dioxide, water, nitrogen, carbon monoxide and other trace components. The hydrocarbon reformate 28 enters the carbon monoxide removal system or adsorption-catalytic oxidation (ACO) processor 29 where carbon monoxide is extracted from the reformate 28. A substantially carbon monoxide-free reformate 32 from the ACO processor 29 is then channeled to a fuel cell or stack 33 where it is used in the production of a D.C. power 34. The fuel processor 27, the ACO processor 29, and the fuel cell stack 33 can be controlled by a central management system 11.

More specifically, the hydrocarbon fuel 26, such as gasoline, natural gas or methanol, is introduced into the fuel processor 27. While various designs can be used, the fuel processor 27 can preferably be constructed with a design that incorporates steam reforming or partial oxidation stage, high temperature water-gas shift reaction stage, and low temperature water-gas shift reaction stage. The fuel processor 27 converts the hydrocarbon fuel 26 into the hydrocarbon reformate 28 by the receipt of water 12, coolant 15, and/or air 13. Typically, the fuel processor 27 will perform some initial carbon monoxide reduction as a result of the water-gas shift reactions. Additionally, as a result of receiving the water 12, the fuel processor 27 may also condition the humidity and the temperature of the hydrocarbon fuel 27 for subsequent carbon monoxide removal and fuel cell application. Alternatively, the humidification and temperature adjustment can be performed at the exit of ACO processor 29 for optimum fuel cell operation. The coolant 15 is used to regulate the operating temperature of the processor 27.
The air, water and thermal management system 11, such as a computer interfaced with control hardware such as valves, compressors, conduits, etc., controls the flow of the water 12, air 13 and coolant 15 to the fuel processor 27. Operational data 14 that relates to the operating parameters of the fuel processor 27 is exchanged between the management system 11 and the fuel processor 27. Similarly, operational data 16 that relates to the operating parameters of the ACO processor 29 and operational data 19 that relates to the operating parameters of the fuel cell 33 is exchanged with the management system 11. In a preferred embodiment, a single air, water and thermal management system 11 controls the fuel processor 27, the carbon monoxide removal system 29, and the fuel cell stack 33. It is, however, envisioned that multiple control systems could be used to control each of these components.

Upon discharge from the fuel processor 27, the hydrocarbon reformate 28 enters the carbon monoxide removal system or ACO processor 29. The carbon monoxide removal system 29, according to a preferred embodiment of the present invention, comprises a plurality of adsorption-catalytic-oxidation (ACO) beds 30a, 30b, 30c, and 30d (Figure 2a). While Figure 2a depicts only four beds or plug-flow reactors, the present invention contemplates that more or less than four beds can be utilized to practice the invention. As seen in Figure 3, all beds 30a-d are preferably of a plug-flow configuration, although other configurations are contemplated. Also, while the present embodiment includes all beds having the same configuration, the beds 30a-d can each have different configurations.

The bed or reactor 30, as disclosed in Figure 3, has an overall cylindrical configuration. At one end thereof, the reactor 30 includes a reactor inlet 53 that receives either an initial amount of reformate 28 or an oxygen containing gas 24 (such as air), depending on whether the reactor 30 is in a stage of adsorption or regeneration, as described below. The oxygen containing gas or oxidizing gas 24 is preferably heated upstream of the reactor 30 or the ACO system 29 (Figure 2a) by a heating element (not
shown), such as a component of the system 10 that can include the fuel processor 27 or the fuel cell stack 33. The heating element can also be a compressor, a heater or a heat-exchanger, which is controlled by the management system 11. The heat-exchanger can be constructed according to any well-known design such as those listed in "Handbook of Heat and Mass Transfer" N. P. Cheremisinoff eds. Gulf Publishing Co. Houston, Texas, 1986. Examples include tubular or plate-fin type heat-exchangers. The oxidizing gas 24 is pre-heated to a temperature that will optimize the speed and thoroughness of the regeneration of a bifunctional material 45 through the catalytic oxidation of carbon monoxide described below. For this embodiment, the pre-oxidizing gas 24 has a temperature range between about 50°C to 350°C.

In an alternative embodiment, the oxidizing gas 24 is not pre-heated and the reactor 30 thus includes an integral heater or heat-exchanger 51 that is constructed according to any well-known design, such as a coiled resistant heater or a tubular heat-exchanger. In either embodiment, at the end of the reactor 30 that is opposite the inlet 53 an outlet 54 enables a substantially carbon monoxide free reformate 32 or a carbon dioxide-enriched sweep gas 43 to exit the reactor 30.

The ACO beds 30a-d contain the bifunctional material 45 (Figure 4) mentioned above. While the preferred embodiment contemplates each of the beds 30a-d having the same bifunctional material 45, it is also within the scope of the invention that the bifunctional materials 45 in each bed 30a-d are different. In the latter situation, for example, a first bed 30a would contain a first bifunctional material and a second bed 30b would contain a second bifunctional material. In either situation, the material 45 is "bifunctional" in that it acts as an adsorbent of carbon monoxide or an oxidation catalyst, depending on whether the bed 30 is in the adsorption or regeneration phase. The bifunctional material 45 is characterized by a significant difference in Gibbs energy of adsorption between carbon monoxide and hydrogen. As a result, the bifunctional material 45 preferentially chemisorbs carbon monoxide
over hydrogen that is contained in the reformate 28. The term “chemisorbs” herein refers to the quasi-chemical bonding between the bifunctional material 45 and carbon monoxide. Subsequent references herein to “adsorb” and “chemisorb” are used interchangeably.

As depicted in Figure 4, the bifunctional material 45 comprises a highly dispersed active component 50 disposed on a high surface-area support 44, which may, for example, be in the form of a pellet (Figure 3). The support 44 may also rest on the surface of a substrate 46, such as a monolith or ceramic foam (Figure 4). The monolith or ceramic foam 46 may be constructed of various materials such as cordierite, alumina, zirconia, silicon carbide, etc. The active component 50 preferably comprises noble metals such as platinum, palladium, ruthenium, rhodium, iridium, gold and silver. Alternatively, the active component 50 comprises transition metals including, manganese, copper, nickel, cobalt, chromium, and iron. Furthermore, the active component 50 may contain combinations of any of the above metals. But the active component 50 more preferably comprises one or two noble metals and/or one or two transition metals. These metals can be in a zero valance state or oxidized state. For a noble metal based bifunctional material 45, the preferred metal loading range is from about 0.5 wt.% to 15 wt.%. For transition metals, the loading can range from about zero to 100%, but preferably falls in the range of about 0.5 wt. % to 50 wt.%.

As mentioned above, the active component 50 is “highly dispersed” on the support 44. The characteristic of a high dispersion coefficient is intrinsic to the general size and configuration of a particle, not the type of metal used. It is the ratio of the number of surface atoms in a given particle divided by the total number of atoms within the particle. As can be seen from the above formula, the dispersion coefficient is a dimensionless figure. In a preferred embodiment, the dispersion coefficient is between about 15 to 100%. A low dispersion coefficient indicates that only small fraction of the metal atoms are at the surface with poor metal utilization. This usually results in a need of increased metal loading and, hence, an increase in cost. The dispersion
coefficient can be improved by reducing the metal particle size to the point that a majority of the atoms are exposed at the surface of the particles.

The support 44 is preferably a high surface area refractory metal oxide that provides a better environment for dispersing the active component 50 to highly amorphous micro-crystallites. Examples of suitable materials for the support 44 include alumina, titania, silica, zirconia ceria etc.. The characteristic of a high surface area refers to an area to weight ratio and can quantitatively vary. However, in this embodiment, the surface area preferably range from about 20 to 300 m$^2$/g and, more preferably, range from about 100 to 300 m$^2$/g. Below about 20 m$^2$/g, the surface area may not be sufficient to disperse the active component 50 to fine particles.

From the above discussion, it can be understood that during the absorption phase of a single reactor 30, an initial amount of reformate 28 passes through the catalyst layer or bifunctional material 45 and the carbon monoxide in the reformate 28 is chemisorbed. Substantially carbon monoxide-free reformate 32 (Figures 1 and 3) is then discharged through the reactor outlet 54. Over time and in the process of adsorbing carbon monoxide, the bifunctional material 45 eventually approaches a point of carbon monoxide saturation, thereby reducing or altogether eliminating its capacity to adsorb additional carbon monoxide from the reformate 28. To allow the bifunctional material 45 to maintain an effective adsorption of carbon monoxide, the carbon monoxide must, from time to time, be removed from the bifunctional material 45, thereby regenerating the adsorption capacity of the bifunctional material 45. The regeneration preferably occurs prior to the time the bifunctional material 45 reaches carbon monoxide saturation and, more preferably, before there is any substantial degradation of the ability of the bifunctional material 45 to adsorb carbon monoxide.

During the regeneration phase of the reactor 30, the flow of reformate 28 through the bifunctional material 45 is stopped. Then, an oxidant, such as the air 24, flows through the bifunctional material 45. In the event the air 24 has been pre-heated, the pre-heated air 24 sweeps across the bifunctional
material 45, oxidizing the carbon monoxide to carbon dioxide. Because carbon dioxide has a relatively low Gibbs energy of adsorption over the bifunctional material 45, it is easily released by the bifunctional material 45 and swept away by flow of pre-heated air or sweep gas 24. With the adsorbed carbon dioxide now released, the bifunctional material 45 is again able to adsorb additional carbon monoxide. Thus, the adsorption capacity of the bifunctional material 45 has been regenerated. At the same time, a carbon dioxide-enriched sweep gas is discharged from the ACO system 29.

The preferred embodiment envisions the timing of the adsorption-regeneration cycle to be controlled by the management system 11. In determining the timing of the cycle, the management system 11 will evaluate data including the amount of carbon monoxide or carbon dioxide detected at the exits of the fuel processor 27 and the ACO system 29, as well as the flow rate, temperature, etc. A sensing device, such as a broadband infrared adsorption detector, could be used for such detection, with the information to be used as part of the operational data 14, 16, and 19 to the management system 11.

It can be seen that the adsorption-regeneration cycle in a single reactor 30 comprises the steps of sequentially adsorbing carbon monoxide from the hydrocarbon reformate 28 by means of the bifunctional material 45 and regenerating the bifunctional material 45 by means of the heated air 24 sweeping through the bifunctional material 45. For increased efficiency, an ACO system 29 having multiple beds 30 can be used, as shown in Figure 2a. These individual beds 30 can be connected in either a series or parallel flow configuration, depending on the application need. For example, the multiple beds 30 can be flow connected in series when maximizing the utilization of the capacity of each bed 30 is necessary, such as the configuration shown in Figure 2a. However, the beds 30 can be flow connected in parallel when minimizing the pressure drop across the ACO system is important. With "N" being the number of beds in the ACO system 29, the beds 30 can be sequentially or serially operated at 360°/N out-of-phase with each other. For
example, each bed 30 can be sequentially regenerated one at the time, following the saturation of the previous one.

As a specific example of four beds 30 being sequentially operable, Figures 2a-d depict the beds 30 flow connected in series. In Figure 2a, and at one point in time of an adsorption-regeneration cycle, the air 24 flows into the first reactor 30a which is in a regeneration phase. Thus, as the carbon monoxide adsorbed on the first bifunctional material 45 is oxidized to carbon dioxide, the air or sweep gas 24 carries the carbon dioxide out of the first reactor 30a as a carbon dioxide or sweep gas exhaust 43. Concurrently, the reformate 28 flows into the second reactor 30b which is in an adsorption phase. Accordingly, the second bifunctional material 45 in the second reactor 30b adsorbs carbon monoxide in the reformate 28, which then enters a conduit 42d. The conduit 42d enables the reformate 28 to flow from the second reactor 30b to the third reactor 30c. The third reactor 30c is also in an adsorption phase and so adsorbs carbon dioxide from the reformate 28 that was not absorbed by the second reactor 30b. A conduit 41d allows the reformate 28 to flow from the third reactor 30c and into the fourth reactor 30d which is in an adsorption phase. Consequently, the fourth reactor 30d adsorbs carbon monoxide in the reformate 28 that was not absorbed by the second and third reactors 30b,c. From the fourth reactor 30d, the carbon monoxide free reformate 32 exits. In still referring to Figure 2a, the dashed lines with arrows depicts the reactors 30a-d being positionally changed to change a reactor, for example, from a regeneration phase to an adsorption phase.

The positional change of the reactors 30a-d is accomplished, according to one embodiment of the present invention, by an inlet valve assembly 41 and an outlet valve assembly 42, as shown in Figures 2b-d. The inlet valve assembly 41 includes a first inlet manifold 41a that is rotationally fixed about the longitudinal axis of the ACO processor 29. A second inlet manifold 41b is juxtaposed to the first inlet manifold 41a, but is rotatable about the longitudinal axis of the ACO processor 29. Both of the first and
second inlet manifolds 41a,b describe four apertures 41c that allow flow communication between the manifolds 41a,b and the four reactors 30a-d. The conduit 41d flow connects the third and fourth reactors 30c,d in this embodiment.

The inlet valve assembly 41 is fixed to a first inlet 35 and a second inlet 36. For the embodiment shown in Figures 2a-d, the first inlet 35 enables the reformate 28 to flow through a control valve 37, into the first inlet 35, and enter the second reactor 30b. The second inlet 36 enables the air 24 to flow through a control valve 38, into the second inlet 36, and enter the first reactor 30a.

Similar to the inlet valve assembly 41, the outlet valve assembly 42 includes a fixed, first outlet manifold 42a and a rotatable second outlet manifold 42b. Both manifolds 42a,b describe four apertures 42c that allow flow communication between the manifolds 42a,b and the four reactors 30a-d. The conduit 42d, in this embodiment, provides flow communication between the second and third reactors 30b,c. As shown in Figures 2c and 2d, the outlet valve assembly 42 communicates with a first outlet 39 which enables the carbon monoxide free reformate 32 to exit from the fourth reactor 30d. The valve assembly 42 also communicates with a second outlet 40 which enables the sweep gas exhaust to exit from the first reactor 30a.

In operation, it can be seen that when the first reactor 30a has completed its regeneration phase, all four reactors 30a-d can be rotated by rotation of the second inlet manifold 41b and the second outlet manifold 42b. Doing so changes the position of the reactors 30a-d relative to the first inlet inlet manifold 41a and the first outlet manifold 42a. With such positional change, the second reactor 30b can, for example, take the original position of the first reactor 30a. So changed, the second reactor 30b can undergo a regeneration phase and the first reactor 30a can undergo an adsorption phase.

It should be understood that the embodiment disclosed in Figures 2a-d is not intended to limit the use of valves and manifolds. For example, multiple
independent valve assemblies could independently control the air 24 and the reformate 28 entering and exiting multiple ACO beds 30a-d. Likewise, multiple, separate conduits for the heated air 24 and the reformate 28 could enter an ACO bed 30 at separate locations, or be channeled into a single input conduit by means of an input manifold. Finally, it should be understood noted that manifolds could be utilized to independently channel the reformate 28 and/or heated air 24 from a common source to a plurality of ACO beds 30.

As a result of alternating flows of the pre-heated air 24 and reformate 28 across a particular bed 30, the simultaneous oxidation of hydrogen, such as that observed in PROX method, is greatly minimized. For the preferred embodiment, parasitic hydrogen consumption, which is mainly caused by the trapping of residual hydrogen in the ACO reactor 30 void space during the cycle switching is less than about 0.1%. As can be appreciated, the adsorption-regeneration cycle can be operated continually. After exiting the ACO system 29, the carbon monoxide-free reformate 32 enters a fuel cell 33, where it is converted into electrical energy 34 (Figure 1).

The fuel cell stack 33, as shown in Figure 1, interfaces with the management system 11 to receive humidified air 17, coolant 18, and water 20. The air 17 serves as an oxidant to the fuel cell stack 33, the coolant 18 serves to regulate the operating temperature of the fuel cell stack 33, and the water 20 serves to further humidify the CO-free reformate 32 to nearly 100% humidity at the operating temperature of the fuel cell stack 33. During operation of the fuel cell stack 33, an oxygen depleted air 21 from the fuel cell stack 33 , together with a hydrogen depleted reformate 22, will be redirected by the management system 11 to be further treated before they can be released through the exhaust 23.

EXAMPLES

Figure 5 is a graph of carbon monoxide concentration versus time according to one embodiment of the present invention. An adsorbent/catalyst
with approximately 6 wt. % Pt over Al$_2$O$_3$ was prepared by the wet incipient method, which is well known in the art and described, for example, in “Heterogeneous Catalysis in Industrial Practice” by Charles N. Satterfield, McGraw-Hill, New York, 1991. The adsorbent/catalyst was subsequently calcined at about 250 to 500°C and reduced in hydrogen at about 200 to 450°C. About 3.22 g of the adsorbent/catalyst was packed into an ACO bed with a plug flow reactor configuration. The packing volume was 10 cubic centimeter (cc). A mixture of synthetic reformate containing 123 ppm carbon monoxide, 19.59% carbon dioxide, 37.06% hydrogen (H$_2$), 20% H$_2$O, and the balance nitrogen (N$_2$) was channeled through the ACO plug flow reactor at 80°C and a flow rate of 2 liters per minute. The effluent from the ACO reactor was directed to carbon monoxide and carbon dioxide non-dispersive infrared (NDIR) detectors downstream from the reactor, thus the change of carbon monoxide and carbon dioxide concentrations could be monitored constantly. The concentrations of carbon monoxide and carbon dioxide are disclosed in Figure 5. During the adsorption cycle, carbon monoxide in the reformate was completely removed until the ACO reactor was saturated. The non-zero baseline for carbon monoxide shown in Figure 5 was due to the infrared absorption interference from excess amounts of carbon dioxide present. The level profile of carbon monoxide from roughly 100 seconds to roughly 750 seconds demonstrates a thorough adsorption of carbon monoxide by the Pt/Al$_2$O$_3$ catalyst. The steady rise in carbon monoxide levels from about 750 seconds to about 1200 seconds indicates that as the bifunctional material approached saturation, its adsorption capacity was steadily reduced. After near complete breakthrough of carbon monoxide was observed at ~1200 seconds, the stream of reformate was diverted from the plug flow reactor, and hot air at 80°C was introduced. Instantaneous carbon monoxide oxidation was observed, as indicated by the robust formation of carbon dioxide at roughly 1450 seconds. An extremely thorough and rapid oxidation of carbon monoxide occurred, as evidenced by the narrow profile of the carbon dioxide peak.
Figure 6 is a graph of carbon monoxide concentration versus time according to another embodiment of the present invention. An adsorbent/catalyst with a metal loading of 7 wt.% Pd over γ-Al₂O₃ was prepared by the wet incipient method. The bifunctional material was packed into an ACO reactor with the similar volume as that described for Figure 5. A mixture of synthetic reformate containing 123 ppm carbon monoxide, 19.59% carbon dioxide, 37.06% hydrogen (H₂), 20% H₂O, and the balance nitrogen (N₂) was channeled through the ACO plug flow reactor at 80°C and a flow rate of 2 liters per minute. The effluent from the ACO was directed to carbon monoxide and carbon dioxide NDIR detectors downstream from the catalytic layer in the ACO. The change in concentrations of carbon monoxide and carbon dioxide are disclosed as graphs in Figure 6. The test results were very similar to those disclosed in Figure 5, further demonstrating the complete removal of CO during the adsorption cycle and rapid CO oxidation during the oxidation cycle.

Figure 7 is a graph of carbon monoxide concentration versus time according to yet another embodiment of the present invention. An adsorbent/catalyst with a metal loading of 3.5 wt.% Ru over γ-Al₂O₃ was prepared by the wet incipient method. Approximately 3.2 grams of the bifunctional material was packed into a 10 cc ACO reactor. A mixture of synthetic reformate containing 1500 ppm carbon monoxide, 19.59% carbon dioxide, 37.06% hydrogen (H₂), and the balance nitrogen (N₂) was channeled through the ACO plug flow reactor at 120°C and a flow rate of 1 liters per minute. The effluent from the ACO was directed to carbon monoxide and carbon dioxide NDIR detectors downstream from the catalytic layer in the ACO. Four consecutive adsorption/regeneration cycles were demonstrated by the change of CO and CO₂ concentrations in Figure 7. During each cycle, the carbon monoxide was nearly completely removed from the reformate stream through the selective adsorption over ACO bifunctional material surface. At about 10% CO breakthrough point of each adsorption cycle, air was introduced to quickly oxidize the adsorbed CO to CO₂. The
adsorption/regeneration cycles were highly repeatable, as demonstrated by
the four cycles in Figure 7.

An additional test was performed wherein 10 grams of a high surface
area catalyst comprising Carolite 300 from Carus Corp. was used. The
catalyst includes a mixture of several amorphous metal oxides such as MnO₂,
CuO and Al₂O₃. The temperature of the ACO bed was kept at 80°C during
the adsorption cycle and 120°C during the oxidation cycle. A synthetic
reformate comprising 1250 ppm carbon monoxide, 19.59% carbon dioxide,
37.06% hydrogen (H₂) and the balance nitrogen was channeled at 1.2 liters
per minute through the ACO bed. Both carbon monoxide and carbon dioxide
were monitored downstream of the bed with NDIR detectors. The test results
were similar to those in Figure 5, suggesting that the catalyst had a capacity
of about 0.6 mmole CO/gram under the above operating conditions.

As can be appreciated by those skilled in the art, the present invention
provides a new approach to improve fuel cell operation efficiency by removing
carbon monoxide from the hydrogen fuel externally. The present invention
has advantages of a high degree of CO removal, simple system configuration,
low parasitic hydrogen consumption and more tolerance to the dynamic
variation of CO output from the reformer. Additionally, this invention may be
used on a wide range of fuel cells which performance may be negatively
affected by the presence of carbon monoxide. Although an important
application of this invention is to eliminate the CO low concentration from the
hydrogen fuel for fuel cell operation, there is no limitation on the type of
application that can be derived from this invention.

It should be understood, of course, that the foregoing relates to
preferred embodiments of the invention and that modifications may be made
without departing from the spirit and scope of the invention as set forth in the
following claims.
WE CLAIM:

1. A method of reducing carbon monoxide from a hydrocarbon reformate, comprising the steps of:
   moving an initial amount of said reformate through a first bed comprising a bifunctional material that preferentially adsorbs carbon monoxide;
   preferentially adsorbing said carbon monoxide by said bifunctional material such that an adsorption capacity of said bifunctional material is reduced;
   restricting an additional amount of said reformate from moving through said first bed;
   passing an oxidizing gas through said first bed; and
   converting said carbon monoxide to carbon dioxide, thereby regenerating said adsorption capacity of said bifunctional material.

2. The method of Claim 1 wherein the step of restricting an additional amount of said reformate bed occurs before carbon monoxide saturation of said bifunctional material has been reached.

3. The method of Claim 1, further comprising the step of moving an initial amount of said reformate through "N" number of beds that are disposed in one of series flow and parallel flow configuration.

4. The method of Claim 1, further comprising the steps of:
   restricting an additional amount of said oxidizing gas through said first bed; and
   restoring the movement of said reformate through said first bed.

5. The method of Claim 1, further comprising the step of removing said carbon dioxide from said first bed by exhausting said oxidizing gas from said first bed.
6. The method of Claim 1 wherein said bifunctional material comprises an active component selected from a group consisting of noble metals and transition metals.

7. The method of Claim 1 wherein said bifunctional material comprises a support selected from the group consisting of alumina, titania, silica, ceria, and mixtures thereof.

8. The method of Claim 1 wherein said bifunctional material comprises a substrate selected from the group consisting of cordierite, alumina, zirconia, and silicon carbide.

9. A method of reducing carbon monoxide from a hydrocarbon reformate, said method comprising the steps of:
   sequentially channeling an initial amount of said reformate into a plurality of reactors comprising a bifunctional material;
   preferentially chemisorbing said carbon monoxide by said bifunctional material such that a chemisorption capacity of said bifunctional material is reduced;
   passing a pre-heated oxidizing gas sequentially through said reactors;
   converting said carbon monoxide to carbon dioxide; and sequentially regenerating said chemisorption capacity of said bifunctional material in said reactors.

10. The method of Claim 9 wherein said reactors are disposed in one of a series flow configuration and a parallel flow configuration.
11. The method of Claim 9 wherein the step of sequentially regenerating said chemisorption capacity comprises the steps of:
sequentially restricting an additional amount of said reformate into said reactors; and
sequentially removing said carbon dioxide from said reactors by exhausting said oxidizing gas from said reactors.

12. The method of Claim 9 wherein the step of restricting an additional amount of said reformate occurs before substantial degradation in an adsorption capacity of said bifunctional material.

13. The method of Claim 9 wherein said bifunctional material comprises an active component present between about 0.5 to 15 wt.%.

14. The method of Claim 9 wherein said bifunctional material comprises a support characterized by a surface area between about 20 to 300 m$^2$/g.

15. A method of providing D.C. power from a hydrocarbon reformate containing carbon monoxide, comprising the steps of:
processing a hydrocarbon fuel in a fuel processor to form said reformate containing carbon monoxide;
sequentially channeling an initial amount of said reformate containing carbon monoxide into a plurality of reactors comprising a bifunctional material that preferentially adsorbs said carbon monoxide;
sequentially adsorbing said carbon monoxide by said reactors;
passing a pre-heated oxygen containing gas sequentially through said reactors; and
sequentially catalyzing a conversion of said carbon monoxide adsorbed on said bifunctional material to produce a substantially carbon monoxide free reformate; and
passing said carbon monoxide free reformate into a fuel cell to produce said D.C. power.

16. The method of Claim 15, further comprising the steps of: sequentially restricting an additional amount of said reformate containing carbon monoxide to said reactors; sequentially restricting an additional flow of said pre-heated oxygen containing gas through said reactors; and sequentially restoring a flow of said reformate containing carbon monoxide through said reactors.

17. The method of Claim 15, wherein said reactors are in one of a series flow configuration and a parallel flow configuration.

18. An adsorption-catalytic oxidation processor system for removing carbon monoxide from a hydrocarbon reformate, said system comprising:

a first bed comprising a first bifunctional material having a first active component that preferentially adsorbs said carbon monoxide from said reformate;

a second bed comprising a second bifunctional material having a second active component that preferentially adsorbs said carbon monoxide from said reformate;

an inlet valve assembly operatively connecting said first and second beds, said inlet valve assembly for rotating said first and second beds and thereby sequentially channeling said reformate and an oxidizing sweep gas between said first and second beds;

a heating element for heating said oxidizing sweep gas; and an outlet valve assembly operatively connecting said first and second beds, said outlet valve assembly for rotating said first and second beds and thereby sequentially channeling a substantially carbon monoxide free reformate from said first and second beds.
19. The system of Claim 18 wherein said heating element is disposed upstream to said first and second beds.

20. The system of Claim 19 wherein said heating element is one of a fuel processor and a compressor

21. The system of Claim 18 wherein said heating element is integral to one of said first and second beds.

22. The system of Claim 21 wherein said first and second beds each comprise a heating element.

23. The system of Claim 18 wherein said inlet valve assembly prevents a simultaneous receipt of said reformate and oxidizing sweep gas by any one of said first and second beds.

24. The system of Claim 18 wherein said outlet valve assembly sequentially channels a carbon dioxide containing sweep gas from said first and second beds.

25. A carbon monoxide removal system, comprising:
   a fuel processor that processes a hydrocarbon fuel containing said carbon monoxide;
   an adsorption and catalytic oxidation processor downstream of said fuel processor, said processor comprising a plurality of reactors, said reactors comprising a bifunctional material having an active component and a support, said bifunctional material adsorbing said carbon monoxide preferentially over hydrogen in said fuel and catalyzing a reaction between said carbon monoxide and an oxygen containing sweep gas; and
   a heating element for heating said oxygen containing sweep gas prior to said sweep gas entering said processor.
26. The system of Claim 25, further comprising a management system that controls said fuel processor and catalytic processor.
FIG. 2a

AIR IN

REFORMATE IN

30a

30b

30c

30d

AIR + CO₂ OUT

CO-FREE REFORMATE OUT

24

43

28

41d

42d
FIG. 5

![Graph showing adsorption and regeneration cycles with CO$_2$ and CO concentrations.]

FIG. 6

![Graph showing adsorption and regeneration cycles with CO$_2$ and CO concentrations.]

SUBSTITUTE SHEET (RULE 26)
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01M/06 C01B3/58

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)
IPC 7 H01M C01B

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>EP 0 750 361 A (EXXON RESEARCH ENGINEERING CO) 27 December 1996 (1996-12-27)</td>
<td>1-17</td>
</tr>
<tr>
<td></td>
<td>column 1, line 3 - line 22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>column 2, line 28 - line 42</td>
<td></td>
</tr>
<tr>
<td></td>
<td>column 3, line 7 - line 26</td>
<td></td>
</tr>
<tr>
<td></td>
<td>column 3, line 33 - column 4, line 31; figures 1,2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>&amp; US 5 604 047 A</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>cited in the application</td>
<td>1-8</td>
</tr>
<tr>
<td></td>
<td>PATENT ABSTRACTS OF JAPAN</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>vol. 015, no. 478 (C-0891), 4 December 1991 (1991-12-04)</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>&amp; JP 03 208801 A (MITSUBISHI HEAVY IND LTD), 12 September 1991 (1991-09-12)</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>abstract</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of box C. Patent family members are listed in 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 doubt 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

"P" 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

"R" 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.

"S" document member of the same patent family

Date of the actual completion of the international search
24 January 2000

Date of mailing of the international search report
01/02/2000

Name and mailing address of the ISA
European Patent Office, P. B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-3040, Tx 31 651 epo nl
Fax: (+31-70) 340-3016

Authorized officer
Cubas Alcaraz, J

Form PCT/ISA2/10 (second sheet) (July 1992)
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>WO 93 19005 A (INT FUEL CELLS CORP) 30 September 1993 (1993-09-30) page 9, line 3 - page 11, line 19; claim 1; figure 1</td>
<td>18-26</td>
</tr>
<tr>
<td>A</td>
<td>GB 1 116 585 A (ENGELHARD MINERALS &amp; CHEMICALS) 6 June 1968 (1968-06-06) page 2, line 68 - line 125</td>
<td>9-26</td>
</tr>
</tbody>
</table>
# INTERNATIONAL SEARCH REPORT

**Information on patent family members**

<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CA 2174374 A</td>
<td>24-12-1996</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 69604340 D</td>
<td>28-10-1999</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 9010538 A</td>
<td>14-01-1997</td>
</tr>
<tr>
<td>JP 03208801 A</td>
<td>12-09-1991</td>
<td>NONE</td>
<td></td>
</tr>
<tr>
<td>WO 9319005 A</td>
<td>30-09-1993</td>
<td>DE 69325092 D</td>
<td>01-07-1999</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 69325092 T</td>
<td>30-09-1999</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 0631564 A</td>
<td>04-01-1995</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 5330727 A</td>
<td>19-07-1994</td>
</tr>
<tr>
<td>GB 1116585 A</td>
<td>06-06-1968</td>
<td>NL 6712670 A,B</td>
<td>18-03-1969</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BE 703883 A</td>
<td>01-02-1968</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FR 1526930 A</td>
<td>12-11-1969</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 1567492 A</td>
<td>13-08-1970</td>
</tr>
</tbody>
</table>