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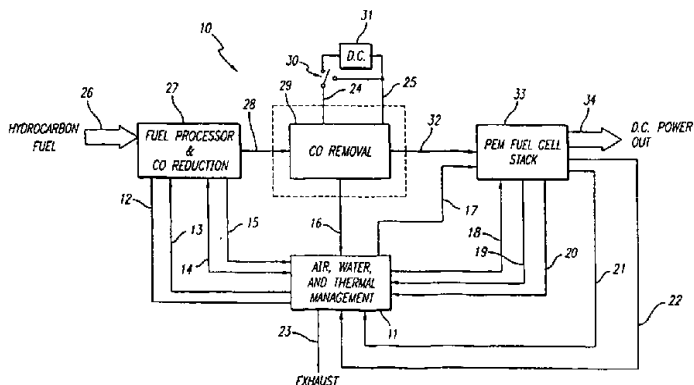
(57) Abstract

A method and apparatus removes carbon monoxide from hydrogen rich fuel by means of a catalytic material that preferentially adsorbs carbon monoxide. The catalytic material is regenerated by an oxidizing agent that reacts with the carbon monoxide absorbed by the catalytic material. The reaction is initiated by an electrical current is generated either galvanically or electrolytically through the catalytic material. The carbon monoxide free gas thus produced may then be passed into a fuel cell in order to provide D.C. power.

ABSTACT

A method and apparatus 10 removes carbon monoxide from hydrogen rich fuel by means of a catalytic material that preferentially adsorbs carbon monoxide. The

5 catalytic material is regenerated by an oxidizing agent 26 that reacts with the carbon monoxide absorbed by the catalytic material. The reaction is initiated by an electrical current which is generated either galvanically or electrolytically through the catalytic material. The carbon monoxide free gas 32 thus produced may then be passed into a fuel cell 33 in order to provide D.C. power 34.

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ELECTROCATALYTIC METHOD AND DEVICE FOR REMOVING CARBON MONOXIDE FROM HYDROGEN-RICH GAS

CROSS-REFERENCE TO RELATED APPLICATIONS

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This application is based upon U.S. Provisional patent application no. 60/100,990, filed September 18, 1998.

BACKGROUND OF THE INVENTION

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This invention relates to carbon monoxide removal from a hydrocarbon reformate fuel. More specifically, it relates to apparatus and methods that use a catalytic material to adsorb carbon monoxide and an electrical current to initiate a chemical reaction between an oxidizing agent and carbon monoxide that has been adsorbed by the catalytic material, thereby regenerating the 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 efficiency and utilizing renewable energy resources.

Fuel cells convert the chemical energy in the fuel directly into electrical energy through an electro-chemical reaction. Because they do not operate

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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

5   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, hydrocarbon, nitrogen oxide and carbon monoxide emissions are negligible,

10 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

15 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,

20 such as gasoline and methanol, is expected to be utilized. However, these fuels usually contain 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 efficient operation of a fuel cell, even relatively low concentrations of carbon monoxide can

25 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.

Prior attempts to remove carbon monoxide from a gas mixture include

30 a pressure swing adsorption method disclosed in Nishida et al., U.S. Patent no. 4,743,276. They disclose a method for selectively absorbing carbon monoxide by means of Cu(I) disposed on a zeolite support, including the step

of adiabatically compressing a gas mixture in the pressure range of 0.5 kg/cm^2 to 7 kg/cm^2. Golden et al., U.S. Patent no. 5,531,809 disclose a vacuum swing method as a variation of the pressure swing method disclosed in Nishida. A solid absorbent is selected which physically absorbs carbon

5   monoxide under pressure. When the pressure is reduced to the range of approximately 20 to 100 torr, the carbon monoxide is released from the solid absorbent. By cyclically repeating this process, carbon monoxide may be removed from a gas.

There are, however, multiple limitations to applying the pressure swing

10   adsorption method to fuel cell applications. Firstly, bulky and expensive pressure resistant tanks, as well as pressure and vacuum pump apparatus, are required to carry out the process. The parasitic weight and volume of these devices make it extremely difficult to apply the pressure swing adsorption method for transportation applications such as a fuel cell power

15   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

20   desorption has to be converted to carbon dioxide with additional process steps and equipment.

Another prior art process has been referred to as preferential catalytic oxidation (PROX) of carbon monoxide which was documented in U. S. Patent no. 5,271,916 by Vanderborgh et. al. In the PROX process, a small amount

25   of pure oxygen or air is mixed into the reformate fuel before it enters a one - or multiple stage catalytic reactor. The catalyst in the reactor, which usually contains dispersed precious metals such as platinum, ruthenium, iridium, etc., preferentially reacts with carbon monoxide and oxygen to convert them to carbon dioxide. Due to the limited selectivity, however, more than a

30   stoichiometric amount of oxygen is needed to reduce carbon monoxide to an acceptable level. Also, the excess oxygen will oxidize the hydrogen in the reformate fuel. Even with the PROX process, the concentration of CO in the

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reformate stream is often still significantly higher than the desirable level for sustainable PEFC operation. Furthermore, the carbon dioxide in the reformate may be converted to carbon monoxide through a reversed water-gas shift reaction inside of the fuel cell.

5   To further eliminate residual carbon monoxide that escapes from the pretreatment or forms from the reversed water-gas-shift reaction inside of the fuel cell, a direct oxygen injection to fuel cell method was developed. For example, Gottesfeld, U.S. Patent no. 4, 910,099 discloses a method of injecting a stream of oxygen or air into the hydrogen fuel so as to oxidize the

10   carbon monoxide. Pow et al., U.S. Patent no. 5,316,747 disclose a similar means of eliminating carbon monoxide directly by introducing pure oxygen or an oxygen containing gas along the latter portion of a reaction chamber in an isothermal reactor in the presence of a catalyst that enhances the oxidation of the carbon monoxide. Wilkinson et al., U.S. Patent no. 5,482,680 disclose

15   the removal of carbon monoxide from a hydrogen fuel for a fuel cell by means of introducing a hydrogen rich reactant stream into a passageway having an inlet, an outlet and a catalyst that enhances the oxidation of carbon monoxide; introducing a first oxygen containing gas stream into the hydrogen rich reactant stream through a first port along the passage way, thereby

20   oxidizing some of the carbon monoxide within the reactant stream; and introducing a second oxygen containing gas at a subsequent point, further oxidizing the remaining carbon monoxide. Wilkinson et al., U.S. Patent no. 5,432,021 similarly oxidize carbon monoxide to carbon dioxide by means of an oxygen containing gas introduced into a hydrogen rich reactant stream in

25   the presence of an unspecified catalyst.

           There are several significant limitations for the PROX process and oxygen injection process. One of these limitations is the parasitic consumption of hydrogen. Due to the limited selectivity, the oxidant injected into a hydrogen rich fuel is always higher than the stoichiometric amount

30   necessary for oxidizing the carbon monoxide. The unreacted oxygen will consume hydrogen in the stream to therefore reduce the overall fuel efficiency. Another significant limitation of these methods is their 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 in both approaches. Yet, the CO input level often varies as the result of change of the fuel cell power output and, thus, the reformate

5   throughput. It is difficult to constantly match the CO input level with the oxygen level in a dynamic environment. Consequently, unreacted CO will exceed the fuel cell tolerance level, leading to poor performance. Yet another limitation of these two approaches is the concern over safety. The oxygen to hydrogen ratio in the mixture has to be strictly controlled below the explosion

10   threshold.

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

15   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

20   separation process which results in parasitic power loss and equipment complexity.

Methanization is another prior art process to remove carbon monoxide through the catalytic reaction of carbon monoxide with hydrogen to form methane. An example of this method is given by Fleming et. al., U. S. Patent

25   no. 3,884,838. Methane does not have a detrimental impact and is regarded as non-reactive in the fuel cell. The methanation reaction, however, requires hydrogen as a reactant and, therefore, increases the parasitic consumption of the fuel for the fuel cell. Furthermore, under the methanation condition, not only carbon monoxide but also carbon dioxide participates in the reactions.

30   The reaction of carbon dioxide with hydrogen generates carbon monoxide through chemical equilibrium. It is therefore difficult to reduce the carbon monoxide level to the desirable limit for PEFC operation.

Because of the sensitive nature of fuel cells, it is vital that carbon monoxide removal approaches 100% efficiency. In addition to the process limitations, such as cost, excess volume and weight, system complexity and high parasitic hydrogen consumption for the above mentioned methods, there is another common shortcoming, i.e., slow response during the cold start of the fuel cell power plant. Most of these approaches need the system to reach a certain temperature before they are operable, which often represents an undesirable delay between start-up and normal operation.

Therefore, there is a need for a method of removing carbon monoxide from a hydrocarbon reformate that is highly efficient, displays enhanced tolerance to carbon monoxide concentration swings, reduces parasitic hydrogen consumption, eliminates venting of carbon monoxide into the atmosphere, can be operated simply and economically, and can operate at the temperature and pressures of a fuel cell, as well as during the start-up mode.

Any discussion of the prior art throughout the specification should in no way be considered as an admission that such prior art is widely known or forms part of common general knowledge in the field.

SUMMARY OF THE INVENTION

It is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative.

According to the invention, there is provided a method of removing carbon monoxide from a hydrocarbon reformate in an electro-catalytic oxidation processor having an anode with a first catalyst disposed therein, a cathode with a second catalyst disposed therein and a proton exchange membrane mounted between the anode and the cathode, said method including the steps of:

a)   moving the reformate across the anode so that the first catalyst adsorbs the carbon monoxide which reduces its carbon monoxide adsorption capacity;

b)   moving an oxidant across the cathode to generate a transient potential between the anode and the cathode; and

c)   electrically connecting the anode and cathode to produce an electric current through the anode and the first catalyst mounted therein, whereby the adsorbed carbon monoxide carbon is converted to carbon dioxide and the carbon monoxide adsorption capacity of the first catalyst increases.

In the preferred embodiment of the present invention, an electrocatalytic oxidation (ECO) processor for removing carbon monoxide from a hydrocarbon reformate comprises a cell containing an electrode catalytic material that preferentially adsorbs and reacts with carbon monoxide. Preferably, an oxidizing agent that reacts

5   with the carbon monoxide absorbed by the catalytic material, typically converting the carbon monoxide to carbon dioxide, regenerates an adsorption capacity of that catalytic material. Preferably, electrical leads disposed on opposite sides of a proton permeable membrane electrode assembly form a circuit capable of discharging a current through the catalytic material, thereby triggering the regeneration process. The circuit may be

10 galvanic in nature, or comprised of a separate D.C. power supply.

A carbon monoxide removal system according to a preferred embodiment of the present invention comprises a fuel processor that processes a hydrocarbon fuel containing carbon monoxide; an electrocatalytic oxidation processor downstream of the fuel processor which is capable of removing carbon monoxide from the fuel by means of

15 a catalytic material that preferentially adsorbs carbon monoxide; and an electrical circuit that produces an electrical current through the catalytic material, thereby converting the carbon monoxide to carbon dioxide through electro-catalytic oxidation and regenerating the catalytic material.

A preferred method for removing carbon monoxide from a hydrocarbon

20 reformate according to this invention comprises the steps of humidifying the reformate; moving the humidified reformate across an electrode catalytic material that preferentially adsorbs carbon monoxide; and producing an electrical current through the catalytic material which triggers a reaction between the adsorbed water as well as the oxidizing species formed from water during the electro-chemical process with the

25 carbon monoxide, thereby converting the carbon monoxide to carbon dioxide and regenerating the catalytic material.

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

30 BRIEF DESCRIPTION OF THE DRAWINGS

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

Figure 2a depicts a membrane electrode assembly (MEA) of an electro-catalytic oxidation (ECO) processor according to one embodiment of the present invention;

Figure 2b depicts a bipolar plate that can be used on anode and cathode sides of 5 the MEA shown in Figure 2a;

Figure 3 is a graph of carbon monoxide and carbon dioxide concentrations at the exit of an ECO device versus time according to a first galvanic embodiment of a method of the present invention wherein carbon

monoxide is present at about 1014 ppm at the inlet and the ECO processor
utilizes platinum-ruthenium (Pt-Ru) as a catalyst;

Figure 4 is a graph of carbon monoxide concentration at the exit of an
ECO device versus time according to a first electrolytic embodiment of a
5   method of the present invention wherein carbon monoxide is present at about
120 ppm at the inlet and the ECO processor utilizes a rhodium (Rh) electrode
catalyst;

Figure 5 is a graph of carbon monoxide and carbon dioxide
concentrations at the exit of an ECO device versus time according to a
10   second galvanic embodiment of a method of the present invention wherein
the ECO processor utilizes ruthenium (Ru) as a catalyst;

Figure 6 is a graph of carbon monoxide and carbon dioxide
concentrations at the exit of an ECO device versus time according to a first
electrolytic embodiment of a method of the present invention wherein the
15   ECO processor utilizes Ru as a catalyst.

DETAILED DESCRIPTION OF THE INVENTION

Figure 1 is a block diagram disclosing the various component parts of
20   one embodiment of a method and a power generation system 10 for
removing carbon monoxide from a hydrocarbon fuel and producing D.C.
power according to the present invention.   In general, a hydrocarbon fuel
source 26, such as gasoline, natural gas or methanol, is introduced into a fuel
processor 27. In the fuel processor 27, the hydrocarbons can react with air or
25   water through partial oxidation or steam reforming to form a reformate mixture
containing hydrogen, carbon monoxide, carbon dioxide, water and other
minor components.   The reformate mixture usually undergoes additional
steps of catalytic reactions, such as a water-gas-shift reaction, to further
promote the reaction between steam and CO to form hydrogen and CO_2.
30   Upon exiting the fuel processor 27, a hydrogen rich reformate 28
containing a small amount of carbon monoxide (usually less than a few
percent) enters an electro-catalytic oxidation (ECO) cell or processor 29

where carbon monoxide is removed from the reformate 28. A carbon monoxide free reformate 32 exits from the ECO processor 29 and enters a fuel cell assembly or stack 33 where the hydrogen in reformate 32 is electrochemically oxidized at an anode by air or oxygen at a cathode to
5   produce a D.C. power output 34. The operation of the fuel processor 27, the ECO processor 29 and the fuel cell stack 33 can be controlled by a central subsystem 11 which manages the necessary air, water and heat, as well as the operation commands for each stage or step in Figure1.

More specifically, the fuel processor 27 converts the hydrocarbon fuel
10   26 to the reformate 28 through multiple steps. These steps consist of fuel reforming which includes steam reforming or partial oxidation, high temperature water-gas-shift reaction, low temperature water-gas-shift reaction, as well as reformate conditioning such as humidification and temperature control through a heat transfer process.

15   In the steam reforming stage, the hydrocarbon fuel 26 reacts with a water steam 12 over a reforming catalyst at an elevated temperature to form a mixture containing mainly hydrogen, carbon monoxide, carbon dioxide and others. This process is endothermic but energy efficient. In place of the steam reforming, a partial oxidation process can be used in which the
20   hydrocarbon fuel 26 reacts with a small amount of oxygen or air 13 to form a mixture of hydrogen, carbon monoxide, carbon dioxide and others. This process is exothermic and self-sustaining but nonetheless less energy efficient.

Following the steam reforming or partial oxidation stage, the gas
25   mixture undergoes high temperature (i.e., about 350 to 550ºC) and low temperature (i.e., about 200 to 300 ºC) water-gas shift reactions in which the carbon monoxide reacts further with additional steam 12 to form hydrogen and carbon dioxide over the water-gas shift catalysts. In the present invention, the water-gas-shift reactions not only improve the overall yield of
30   hydrogen in the fuel processor 27, it also reduces the carbon monoxide concentration to typically less than a few percent in the reformate output 28.

The above fuel reforming and water-gas shift reaction are well known in the art and described, for example, in "Heterogeneous Catalysis in Industrial Practice" by Charles N. Satterfield, Chapter 10, page 419-465, McGraw-Hill, New York, 1991, which is incorporated herein by reference.

5   Following the water-gas shift reaction, the reformate undergoes a conditioning process during which the humidity and temperature of the reformate output 28 is adjusted to be suitable for PEFC application. The humidity adjustment is accomplished by mixing water steam and the temperature adjustment is accomplished by thermal transfer through a heat

10   exchanger. In a preferred operating condition, the temperature of the reformate output 28 should be in the range of about 70 to 100 °C and the humidity should be close to 100% relative humidity (RH) at the corresponding temperature.

The fuel processor 27 is preferably controlled by the central

15   management subsystem 11 as a result of operational data 14 being transmitted therebetween. The central management subsystem 11 may control any number of operational parameters, such as a water vapor flow 12, an air flow 13, and a coolant flow 15 to the fuel processor 27. In a preferred embodiment, a single integrated electronic management subsystem 11

20   controls not only the fuel processor 27, but also the ECO processor 29 and the fuel cell (or fuel cell stack) 33, both of which are further described below. It is, however, envisioned to control these components with separate management subsystems.

Sensing devices (not pictured) well known in the art can be installed in

25   the fuel processor 27, the ECO processor 29, as well as the fuel cell stack 33. These sensors monitor the overall system 10 performance by measuring the parameters which include, but are not limited to, the pressure, temperature, carbon monoxide concentration, output voltage/current, etc. This data will be part of the operational data 14, 16, 19 which will be directed to the

30   management subsystem 11 and receive feedback from the management subsystem 11 for the control of each operation of the unit. Particularly relevant to this invention is the carbon monoxide data collected as part of

each operation data 14, 16, 19. To generate the operational data with respect to carbon monoxide levels, the sensing device according to one embodiment of the present invention is a broad-band infrared absorption-detector, although other similar devices can also be used.

5   The humidified reformate 28 enters an anode side 36 of the ECO cell 29 (FIG. 2a) through a flow field 50 of a bipolar plate 48 (described below). It passes across an electrode catalytic material 47 which includes a catalyst metal component 41 and a catalyst support 42 further described below. Thereby, the catalytic metal component 41 chemisorbs the carbon monoxide 10 in the reformate 28. The reference to "chemisorbs" herein is intended to refer to chemical adsorption where the electronic interaction between CO and the active site in the catalytic metal 41 occurs to form a quasi-chemical bond. Subsequent references herein to "adsorb" and "chemisorb" are used interchangeably unless otherwise specified, such as "physi-adsorption." The 15 chemisorption of carbon monoxide occurs preferentially over hydrogen. This preferential adsorption is due to a significant difference in the Gibbs energies of adsorption between carbon monoxide and hydrogen with the catalytic sites. Consequently, the catalytic metal component 41 preferentially absorbs carbon monoxide despite the composition of the hydrocarbon reformate typically 20 comprising far greater percentages of hydrogen.

      Over time and in the process of adsorbing carbon monoxide, the catalytic metal component 41 eventually approaches a point of carbon monoxide saturation, thereby reducing or altogether eliminating its adsorption capacity to adsorb more carbon monoxide from the reformate 28. To 25 maintain an efficient removal of carbon monoxide from the reformate 28, the catalytic metal component 41, and specifically its adsorption capacity, should be regenerated. The regeneration preferably occurs prior to the time the catalytic metal component 41 reaches carbon monoxide saturation and, more preferably, before there is any substantial degradation of the ability of the 30 catalytic metal component 41 to adsorb carbon monoxide.

      Regeneration can occur by removing the carbon monoxide from the catalytic metal component 41 via an oxidizing agent such as water vapor 12.

Specifically, the water vapor 12 provides transient species such as a hydroxyl radical, a hydrogen peroxide radical, etc. formed during an electrochemical process (described below) when the water 12 is adsorbed over the surface of the catalytic metal 41. Thus, when an oxidizing agent from the activated

5   water vapor 12 chemically reacts with the carbon monoxide that had been adsorbed by the catalytic metal component 41, carbon monoxide is converted to carbon dioxide that is generally not harmful to the performance of the fuel cell 33. The carbon dioxide produced from the oxidation reaction has only weak physi-adsorption (i.e., adsorption due to van der Waals interaction).

10   Therefore, it is easily released by the catalytic metal component 41 and swept away by the continuing flow of reformate 28. With the adsorbed carbon monoxide now removed, the catalytic metal component 41 is again able to adsorb additional carbon monoxide. Accordingly, the adsorption capacity of the catalytic metal component 41 has been regenerated.

15   To initiate the catalytic oxidation reaction between the oxidizing agent 12 and the carbon monoxide, a current is discharged through the area containing the electrode catalytic material 47 and, specifically, the catalytic metal component 41. The current will initiate an electrochemical process which transforms the water vapor 12 adsorbed on the surface of the catalytic

20   metal 41 to highly reactive oxidizing species. Such current discharge can occur in one of two manners. As further described below, the two manners of current discharge are referred to herein as galvanic and electrolytic. Irrespective of the manner of current discharge, during the regeneration period, the catalyzed oxidation reaction produces the carbon dioxide

25   described above.

          The present invention also includes an adsorption cycle which is distinguished from the regeneration cycle by an absence of electrical current flow and thus an absence of catalytic oxidation reactions. Preferably, a regeneration period or cycle alternates with an adsorption period or cycle as

30   the level of carbon monoxide adsorbed to the catalyst metal component 41 rises and falls. In other words, and for example, during the adsorption cycle, the amount of adsorbed carbon monoxide rises towards the maximum

adsorption capacity of the catalytic metal component 41. Before or upon the catalytic metal component 41 reaching saturation, the adsorption cycle stops and the regeneration cycle commences, during which time the amount of adsorbed carbon monoxide falls. As can be appreciated, the alternation of

5   regeneration and adsorption can theoretically continue indefinitely.

Thus, for example, the adsorption cycle is initiated by precluding an electrical current from being developed across the area of catalytic metal component 41. But upon partial or full carbon monoxide saturation of the catalytic metal component 41, an electric current can be discharged through

10   the area of the catalytic metal component 41 to initiate the regeneration cycle. Consequently, during the adsorption cycle, essentially no protons flow across a proton permeable membrane 35 of the ECO processor 29, as further described below. But such proton flow does occur during the regeneration cycle.

15   Accordingly, no hydrogen consumption takes place during the adsorption period. During the regeneration process, however, a residual amount of hydrogen chemisorbed on the surface of an anode 36 (further described below) of the ECO processor 29, as well as in the gas phase in the ECO processor 29, will participate in electrochemical oxidation reactions on

20   the anode 36. The electrochemical oxidation of hydrogen competes with the electrochemical oxidation of carbon monoxide and water, which are adsorbed on the catalytic metal 41. The electro-oxidation of hydrogen results in the formation of protons. The protons migrate across the proton permeable membrane 35 to cathode 37 of the ECO processor 29 and react with reduced

25   oxygen to form water. Since the electro-chemical process occurring during the regeneration period is usually much faster than the cumulative adsorption process, the adsorption period generally comprises a major portion of the overall ECO operation cycle.

During both the regeneration and adsorption cycles, a substantial

30   amount of carbon monoxide is removed from the reformate 32 exiting the ECO processor 29. However, it can be appreciated that during the adsorption cycle, the amount of carbon monoxide in the exit reformate 32 will be rising as

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the adsorption capacity of the catalytic metal component 41 decreases. To prevent the leakage of carbon monoxide in the exit reformate 32, the ECO processor 29 is preferably regenerated so that the adsorption capacity of catalytic metal component 41 can be restored in a timely fashion. In any event, the carbon monoxide-free reformate 32 can then enter the fuel cell stack 33, which can be of any well known design in the art. In the fuel cell stack 33, the reformate 32 can react with an oxidant, such as air 17, through an electrochemical process which produces a D.C. electrical power 34. The fuel cell byproducts that include an oxygen-depleted air 21 and a hydrogen-depleted reformate 22 can then be exhausted by the management subsystem 11 in the form of an exhaust 23.

As mentioned above, Figure 2a depicts the internal structure of a membrane electrode assembly of an ECO processor 29. Figure 2b depicts a bipolar plate 48 that is used on both sides of the membrane electrode assembly of Figure 2a. Thereby, the ECO processor 29 is generally constructed in a fashion similar to well known proton exchange membrane (PEM) fuel cells. Such PEM cells, including the construction of bipolar plates and membrane electrode assemblies, are described in the article "Polymer Electrolyte Fuel Cells" by S. Gottesfeld and T. A. Zawodzinsk in ADVANCES IN ELECTROCHEMICAL SCIENCE AND ENGINEERING, R. C. Alkire, H Gerischer, D. M Kolb and C. W. Tobias eds., Volume 5, page 195-302, Wiley-VCH, Weinheim, Germany, 1997 and incorporated herein by reference. The ECO processor 29 will be typically operated between ambient temperature to about 180ºC and at about 1 to 5 atmospheres of pressure. The ECO cell 29 includes a first portion and a second portion – namely, the anode 36 and the cathode 37 – together with the proton exchange membrane 35 therebetween. Various proton permeable membrane materials which are well known in the art can be used as the proton exchange membrane 35, such as perflourinated polymers like NAFION®.

The carbon monoxide adsorption and electrochemical oxidation occurs on the anode side of the ECO device 29. The anode side consists of the anode 36 and the bipolar plate 48 with the conducting flow field 50. As shown

in Figure. 2a, the electrode catalytic material 47 includes the catalyst metal component 41 dispersed over a conductive high surface area support 42. On one side of the electrode catalytic material 47, and in close contact therewith, is the proton exchange membrane 35. On the other side of the electrode

5   catalytic material 47 is a porous conductive gas diffusion backing material 44. The backing material 44 provides reformate 28 supply to the anode 36 and can be made of conductive materials with a gas diffusion property such as carbon cloths or porous carbon papers. An example of a commercial backing material 44 is ELAT™ made by E-TEK, Inc. The side of the gas diffusion

10   backing material 44 opposite the catalytic material 47 is in close contact with the bipolar plate 48 which is connected to a first conductive lead 24 (not shown). Through the bipolar plate 48 and the first conductive lead 24, electrons are transferred between the anode 36 and an external circuit 40. The backing material 44 can be coated with a hydrophobic coating 45 to

15   prevent local flooding by water from the electrochemical process and from the humidified reformate 28. An example of the hydrophobic material is fluorinated ethylene propylene (FEP).

In operation, the reformate 28 containing carbon monoxide enters the ECO device 29 through an inlet 49 of the bipolar plate 48. The reformate 28

20   follows the flow path or feed channel 50 across a conductive surface 51 and to an outlet or exhaust 52. During the process, the reformate 28 will also pass through the gas diffusion backing material 44 and interact with the catalyst metal component 41. As it was mentioned earlier, the carbon monoxide in the reformate 28 will be selectively chemisorbed over the catalyst metal

25   component 41. The majority of the carbon monoxide at the outlet 49 of the bipolar plate 48 is therefore being removed from the reformate 28.

To facilitate the proton transfer process during the regeneration cycle, the catalyst metal material 41 and support 42 are bound to the proton exchange membrane 35 in a matrix of proton conductive ionomer composite

30   43. The ionomer composite 43 is generally recasted from the perfluorinated sulfonic acid polymer particles. An example would be NAFION® particles. Alternatively, the catalyst metal material 41 and support 42 can be bound to

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the backing material 44 through the matrix of proton conductive ionomer composite 43 and collectively pressed against the proton exchange membrane 35 upon assembling of the ECO processor 29.

5   The cathode 37 is preferably of design similar to the anode 36 to insure that an oxidant such as oxygen is channeled to interact with the protons traversing the membrane 35.

The catalytic metal component 41 comprises noble and/or transition metals in a highly dispersed form upon the support 42. The support 42 is generally characterized as being electrically conductive, chemically inert, and

10   having a high surface area. The conductivity of the support 42 may vary, but is generally comparable to that of carbon. The need for the suppport 42 to be chemically inert is to avoid reactions between the reformate 28 and the support 42 during both adsorption and regeneration cycles and to maintain the structural stability of the anode 36 during long term ECO process

15   operation. In this embodiment, the surface area of support 42 may range from about 5 to 1500 m^2/g and, more preferably, range from about 150 to 300 m^2/g. Some examples of suitable materials for the support 42 include carbon black, metal nitride and metal carbide such as titanium nitride, tungsten carbide, etc.

20   In another embodiment of this invention, the catalytic metal component 41 can be small metal crystallite powder without a supporting material 42. These metal crystallites are generally highly dispersed with particle dimensions ranging from 10 nm to > 1000 nm. The benefit of using an unsupported metal crystallite is eliminating the requirement and limitation of

25   the support 42. The unsupported metal crystallite, however, generally provides less available surface area than that of supported catalytic metal component 41.

The noble metals that are suitable for use as the catalyst metal component 41 include, but are not limited to, ruthenium, platinum, palladium,

30   rhodium, iridium, gold, silver, etc. The useful transition metals include, but are not limited to, molybdenum, copper, nickel, manganese, cobalt, chromium, tin, tungsten, etc. The present invention contemplates that two

and three noble or transition metals can be used in any combination as the catalytic metal component 41 in the form of a multiple metallic alloy. However, it is preferred that one or two noble metals and/or one or two transition metals be utilized in any form of combinations as a bimetallic alloy,

5   which are demonstrated by the examples below.

Although the catalyst metal component 41 in the anode 36 and the cathode 37 can be the same, catalyst metal component 41 at the cathode 37 is preferably different from that at the anode 36. The preferred catalyst metal component 41 at the cathode 37 include platinum and platinum-transition

10 metal alloys such as Pt-Co, Pt-Cr. The preferred catalyst metal component 41 at the anode 36 is ruthenium, rhodium, iridium, palladium, platinum and their corresponding transition metal alloys.

The performance of ECO processor 29 depends on the amount of catalyst metal component 41 used in the membrane electrode assembly

15 which is normally represented by the weight of the catalyst metal per unit MEA surface area. In this invention, the preferred amount of catalyst metal component 41 for the anode 36 ranges from about 0.1 to 5 mg/cm^2. The preferred amount of catalyst metal component 41 for the cathode 37 ranges from about 0.1 to 5 mg/cm^2.

20 For the catalyst material 47, the amount of catalyst metal component 41 loading in the support 42 can also affect the performance of the ECO processor 29. For a noble metal based catalytic metal component 41, the metal loading over the support 42 preferably ranges from about 2 to 70 wt.%. More preferably, the loading is from about 20 to 50 wt.%. Below about 2

25 wt.%, the net amount of catalyst needed for constructing the anode 36 maybe too high to fully utilize the metal in an electrochemical process where the proton transfer needs to be connected throughout the anode 36. Above 70 wt.%, it is difficult to achieve high metal dispersion which results in lower metal utilization because of the relatively lower surface metal atom to overall

30 metal atom ratio. It is generally believed that the surface metal atoms of the catalyst metal component 41 are the active sites during a catalytic or an electro-catalytic reaction. For a transition metal based catalyst metal

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component 41, the metal loading preferably ranges from about 0 to 40 wt.% and, more preferably, from about 3 to 30 wt.%. Loading outside such range tends to result in similar types of performance degradation described above for noble metals.

5   As noted above, the catalyst metal component 41 is dispersed on the substrate 42 with a high dispersion coefficient. The dispersion coefficient is defined as the ratio of the number of surface atoms of an active catalyst metal to the total number of atoms of the metal particles in the catalyst. In this embodiment, it is preferred that the catalyst metal component 41 be

10   characterized by a dispersion coefficient between about 5 to 100% and, more preferably between about 30 to 90 %. If below about 15%, the catalyst surface area provided by the catalyst metal component 41 can be too low to utilize the catalyst metal efficiently. The low utilization of the catalyst metal can result in a higher amount of the catalyst metal needed for the anode 36,

15   hence leading to a higher cost of the ECO processor 29.

As mentioned above, the regeneration cycle is initiated by a discharge of electrical current through the anode 36 or cathode 37 of the ECO processor 29. Without intending to be limited by any electro-catalysis theory, it is believed that the following chemical and electro-chemical processes

20   occur during the adsorption and the regeneration cycles. During the adsorption stage, the carbon monoxide in the gas phase will chemisorb over the active site of catalyst metal component 41, designated as M, to form a chemisorbed CO species, CO/M, through the reaction:

$$CO + M \rightarrow CO/M \qquad\qquad (1)$$

25   Meanwhile, the hydrogen in the gas phase will also participate in a dissociative adsorption over the active site M through the reaction:

$$H_2 + 2M \rightarrow 2H/M \qquad\qquad (2)$$

Due to the significant difference in the heat of adsorption, the surface concentration of CO/M is higher than that of H/M through the cumulative

30   adsorption of CO. The water vapor in the humidified reformate 28 will also be adsorbed over the surface of the anode 36 to form H_2O_{ads}. The surface on

which the water adsorbs includes, but is not limited to, the surface of active
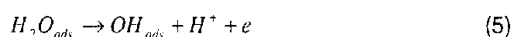site M through the following equation:

$$H_2O(gas) \rightarrow H_2O_{ads} \qquad (3)$$

During the regeneration stage, the following electro-oxidation reactions occur
5   on the surface of the anode 36:

$$H/M \rightarrow M + H^+ + e \qquad (4)$$
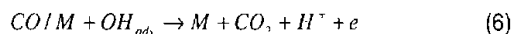
and

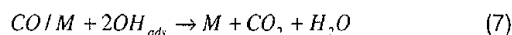$$H_2O_{ads} \rightarrow OH_{ads} + H^+ + e \qquad (5)$$
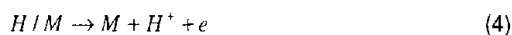
OH_{ads} is the hydroxyl group chemisorbed over the surface of the anode 36
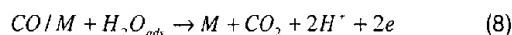10   and which is highly reactive and can oxidize the chemisorbed CO/M through
the following electro-catalytic reaction:

$$CO/M + OH_{ads} \rightarrow M + CO_2 + H^+ + e \qquad (6)$$

or through the direct catalytic reaction:

$$CO/M + 2OH_{ads} \rightarrow M + CO_2 + H_2O \qquad (7)$$

15   Another way to express the electro-catalytic oxidation of chemisorbed carbon
monoxide by water is by the following equation:

$$CO/M + H_2O_{ads} \rightarrow M + CO_2 + 2H^+ + 2e \qquad (8)$$

The carbon dioxide formed through the equations (6) to (8) has a weak
interaction with the anode 36 surface and, therefore, will be swept out of the
20   anode 36 after the regeneration.

Two approaches can be used during the regeneration cycle. They are
galvanic and electrolytic methods. The manner of regeneration is controlled
by the management subsystem 11. For the galvanic approach, the
management subsystem 11 sends a control signal which momentarily closes
25   a double-throw switch 30 between conductive leads 24, 25, as shown in
Figure 1. For the electrolytic approach, the management subsystem 11
sends a control signal which momentarily closes the switch 30 between
conductive leads 24, 25 and a D. C. power supply 31. The leads 24, 25 are
affixed (not shown) to the bipolar plates 48 at both the anode 36 and cathode
30   37 sides of the ECO cell 29. The conductive leads 24, 25 are preferably

connected with the bipolar plates 48 which have an evenly distributed flow field configuration. One such configuration is a serpentine pattern, as is shown in Figure 2b. The bipolar plates have uniform and close contact with the conductive backing material 44 and, therefore, with the anode 36 and

5   cathode 37. The uniform and close contact results in an even flow of electrical current across the catalytic material 47, thereby achieving the most efficient degree of regeneration. Although a timed cycle may be used for the frequency needed for regeneration, the preferred embodiment utilizes measurements or calculations of carbon monoxide levels at the exit of fuel

10 processor 27 and ECO processor 29 to initiate the regeneration cycle.

In the galvanic embodiment, the current is produced exclusively from a galvanic reaction owing to the transient potential difference between the anode 36 and cathode 37 side of the ECO processor 29. The circuit 40 established between the anode 36 and the cathode 37 has a very small or

15 zero resistance. The low impedance allows an instantaneous current to pass between the anode 36 and cathode 37 when the switch 30 closes the circuit. Under such a condition, the carbon monoxide electro-oxidation reaction with water at the anode 36 to form carbon dioxide is accelerated according to the equation (8) listed above. As described above, since the carbon dioxide has

20 a relatively weak adhesion to the anode 36 surface, it can be swept away by the reformate 28 that continues to pass through the ECO cell 29.

In the electrolytic embodiment, the above circuit 40 further comprises a separate power supply or D.C. cell 31, with voltage ranges typically from about 0.1 to 2.0 volts, which applies the external potential and current over

25 the initial discharge of electrical current. When the switch means 30 is closed, the first conductive lead 24 from the anode 36 is operatively connected to a positive terminal of the D.C. cell 31 and the second conductive lead 25 from the cathode 37 is operatively connected to a negative terminal of the DC cell 31. Upon receiving a "reversed" potential from the power

30 supply 31, oxidizing species will be produced as a result of reactions similar to that given in equation (5) above. The oxidizing species include but are not limited to hydroxyl groups, hydro-peroxide groups, etc. These oxidizing

species can be formed over the surface of catalyst metal component 41 or
other parts of the anode 36 and migrate to the catalyst metal component 41.
The oxidizing species can then react with the adsorbed carbon monoxide to
form carbon dioxide. Like in the galvanic embodiment above, the weakly

5   adsorbed carbon dioxide will be stripped by the flow of reformate 28, leaving
the anode 36 surface "clean."

In both galvanic and electrolytic approaches, the duration of the
regeneration is also controlled by the management system 11. The
regeneration duration can be greater than 0 to about 100 seconds. The

10 preferred embodiment of the present invention is from about 0.01 second to
10 seconds.

While the above description deals with a single ECO cell 29, multiple
ECO cells 29 can be used to enhance the overall CO removal capacity.
These multiple ECO cells 29 can be electrically connected in a series or in a

15 parallel pattern, similar to such well known patterns used in fuel cell stacks.
Additionally, and like with fuel cells, the ECO cells 29 can be stacked in a
module wherein the individual cells 29 are electrically connected in series; a
plurality of modules can then be flow connected in parallel. The regeneration
of multiple ECO cells 29 can occur simultaneously or in a sequential manner.

20 However, the sequential manner is preferred. Further, the manner in which
the reformate 28 flows into multiple ECO cells 29 can also be in parallel or in
series, which is also similar to such flows for fuel cell stacks. The series flow
pattern is preferred for more complete carbon monoxide removal.

25   EXAMPLES

Figure 3 graphically discloses test data   wherein an ECO cell was
constructed with a similar configuration as a typical proton-exchange
membrane (PEM) fuel cell. At the anode side of the membrane electrode

30 assembly (MEA), a carbon supported Pt-Ru bimetallic electrode catalyst with
loading of 0.299 mg/cm^2 was attached by the hot-pressed method described
in U.S. Patent no. 5,211,984 and incorporated herein by reference. Similarly,

a Pt/C electrode catalyst with Pt loading of 0.303 mg/cm^2 was attached on the cathode side. The MEA had electrode surface area of 5 cm^2 and the ECO device was operated at 80°C. The anode gas mixture was fully humidified nitrogen containing 1014 ppm carbon monoxide. The gas mixture was

5   introduced through the anode side of the ECO cell at a flow rate of 128 sccm. The cathode gas was fully humidified air at a flow rate of 180 sccm. Separate broad-band IR absorption-detectors were used to monitor carbon monoxide and carbon dioxide levels at the exit of the ECO cell. Figure 3 shows that, at the beginning of the experiment, the carbon monoxide concentration within

10   the gas mixture at the exit decreased significantly as carbon dioxide concentration increased, indicating the selective carbon monoxide adsorption and catalytic oxidation occurring over the electrode catalyst surface. Upon the saturation of carbon monoxide over the anode, gas phase carbon monoxide concentration returned to the original level. At this point, the

15   galvanic regeneration was initiated by electrically shorting the circuit between the anode and cathode for one second to allow the electrocatalytic oxidation to occur at the anode surface. Following the short-circuiting, the carbon monoxide levels in the gas mixture decreased and the carbon dioxide increased, indicating that adsorbed carbon monoxide was oxidized to carbon

20   dioxide and the electrode surface was cleaned for another adsorption cycle. The process was highly repeatable, as seen in Figure 3.

Figure 4 graphically discloses test data in an ECO device similar to that used in Figure 3 and at an operating temperature of 80°C. At the anode side of the membrane electrode assembly, a carbon supported rhodium electrode

25   catalyst with Rh loading of 0.270 mg/cm^2 was attached by the hot-pressed method. Similarly, a Pt/C electrode catalyst with Pt loading of 0.330 mg/cm^2 was attached on the cathode side. During the experiment, a mixture of synthetic reformate mixture containing 120 ppm CO, 19.9% CO_2, 37.0% H_2, balanced by N_2 was fully humidified and passed through the anode side of the

30   ECO cell with a flow rate of 128 sccm while air at essentially 100% relative humidity was passed through the cathode side at a flow rate of 180 sccm. A broad band IR absorption detector monitored the concentration of carbon

monoxide at the exit. At the beginning of the experiment, there was a
significant decrease of carbon monoxide concentration in the reformate flow
at the exit of the ECO cell, indicating a selective carbon monoxide absorption
by the catalytic material within the anode. Upon carbon monoxide saturation

5 of the catalytic material, gas phase carbon monoxide was observed to rise
closely to its original level. At this point, the two electrodes of the ECO cell
were connected to an external DC power supply with 0.4 volts, with the
positive lead of the power supply attached to the anode of the ECO cell and
the negative lead attached to the cathode of the ECO cell, thus producing a

10 "reverse voltage potential." The connection lasted a short period of 1 second
to initiate the electrocatalytic oxidation at the anode surface. As seen in
Figure 4, over repeated cycles, the carbon monoxide levels in the reformate
were reduced through the electrocatalytic oxidation process in a manner
consistent with what would be expected by the regeneration of the catalytic

15 material absorbing the carbon monoxide.

Figure 5 graphically discloses the test results of an experiment with an
ECO cell similar in construction to that used in connection with Figure 3. The
anode electrode catalyst was Ru/C with the ruthenium loading at 0.3 mg/cm^2.
The operating temperature was again 80°C. A fully humidified gas mixture

20 containing 492 ppm carbon monoxide and the balance hydrogen was
introduced into the anode side at a flow rate of 128 sccm. At the same time,
100%-humidified air was passed through the cathode side with a flow rate of
180 sccm. Separate broad band IR absorption detectors monitored carbon
monoxide and carbon dioxide levels at the ECO exit. As shown in Figure 5, at

25 the beginning of the experiment, the carbon monoxide concentration at the
exit decreased while the carbon dioxide concentration increased, indicating
the selective carbon monoxide adsorption and catalytic oxidation occurred
over the electrode catalyst surface. Upon the saturation of the carbon
monoxide over the anode, gas phase carbon monoxide concentration

30 returned to the original level. At this point, the two electrodes of the ECO cell
were connected for one second to allow the electrocatalytic oxidation to occur
at the anode surface. Following this short circuiting, depletion of carbon

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monoxide and enhancement of carbon dioxide in the reformate was observed, indicating that adsorbed carbon monoxide was oxidized to carbon dioxide and the electrode surface was cleaned for another adsorption cycle. The process was highly repeatable, as shown in Figure 5. With an increase

5   of regeneration frequency, such as one second of short circuiting for every 15 seconds of carbon monoxide adsorption, the carbon monoxide level at the exit can be maintained at a constant level, as shown in Figure 5.

Figure 6 graphically discloses the test results with an ECO cell of similar construction and identical chemical concentrations, temperature and

10   humidity as that used to obtain the test results disclosed in Figure 5. The only distinction in the equipment producing the results in Figures 5 and 6 is the addition of an external DC power supply having a potential of 0.4 volts in the tests represented by Figure 6. Upon the saturation of carbon monoxide over the anode, gas phase carbon monoxide concentration returned to the original

15   level. At this point, the two electrodes of the ECO cell were connected to the power supply, with the positive lead of the power supply attached to the anode of the ECO cell and the negative lead attached to the cathode of the ECO cell, thus producing a "reverse voltage potential." Figure 6 illustrates that, when the reverse voltage was applied for approximately one second, the

20   adsorbed carbon monoxide was electrochemically oxidized to carbon dioxide, as indicated by the depletion of carbon monoxide and increase of carbon dioxide at the exit of the ECO device. This process was highly repeatable, as shown in Figure 6. With an increase of the regeneration frequency, such as one second of applying a "reversed voltage" for every 20 seconds of carbon

25   monoxide adsorption, the carbon monoxide level at the exit can be maintained at a constant level, as shown in Figure 6.

As can be appreciated by those skilled in the art, the present invention provides an approach to improve fuel cell operation efficiency by removing carbon monoxide from the hydrogen fuel externally. The present invention

30   provides advantages of a high degree of carbon monoxide removal, simple system configuration, low parasitic hydrogen consumption, increased tolerance to the dynamics of carbon monoxide output from the reformer, and

ease of operation. Although a primary application of the invention is to reduce the concentration of carbon monoxide with the hydrogen fuel for fuel cell operation, the present invention can have other applications where carbon monoxide removal is necessary.

5   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.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1.   A method of removing carbon monoxide from a hydrocarbon reformate in an electro-catalytic oxidation processor having an anode with a first catalyst disposed therein, a cathod with a second catalyst disposed therein and a proton exchange membrane mounted between the anode and the cathode, said method including the steps of:

a)   moving the reformate across the anode so that the first catalyst adsorbs the carbon monoxide which reduces its carbon monoxide adsorption capacity;

b)   moving an oxidant across the cathode to generate a transient potential between the anode and the cathode; and

c)   electrically connecting the anode and cathode to produce an electric current through the anode and the first catalyst mounted therein, whereby the adsorbed carbon monoxide carbon is converted to carbon dioxide and the carbon monoxide adsorption capacity of the first catalyst increases.

2.   The method of Claim 1 further including the step of humidifying the reformate before step (a).

3.   The method of Claims 1-2 further including the step of humidifying the oxidant before step (b).

4.   The method of any one or more of Claims 1-3, wherein the electric current is produced galvanically.

5.   The method of any one or more of Claims 1-3, wherein the electric current is produced electrolytically.

6.   The method of Claims 1-6 wherein the step of electrically connecting further includes the step of electrically disconnecting and then repeating these steps to produce an intermitted electric current.

7.   The method of Claims 1-6 further including the step of augmenting the electric current with a DC power source.

8.   The method of Claims 1-7 wherein said first catalyst is a noble or transition metal and is mounted on a support having a surface area in the range of 5 to 1500 m^2/g.

9.   The method of Claims 1-8 wherein said first catalyst is a noble or transition metal and is mounted on a support having a surface area in the range of 150 to 300 m^2/g.

10.   The method of Claims 1-9 wherein said first and second catalysts are the same noble or transition metal.

11.   A method of removing carbon monoxide substantially as herein described with reference to any one of the embodiments of the invention illustrated in the accompanying drawings and/or examples.

DATED this 21st Day of June 2001
AlliedSignal Inc.

Attorney: PHILLIP D. PLUCK
Fellow Institute of Patent and Trade Mark Attorneys of Australia
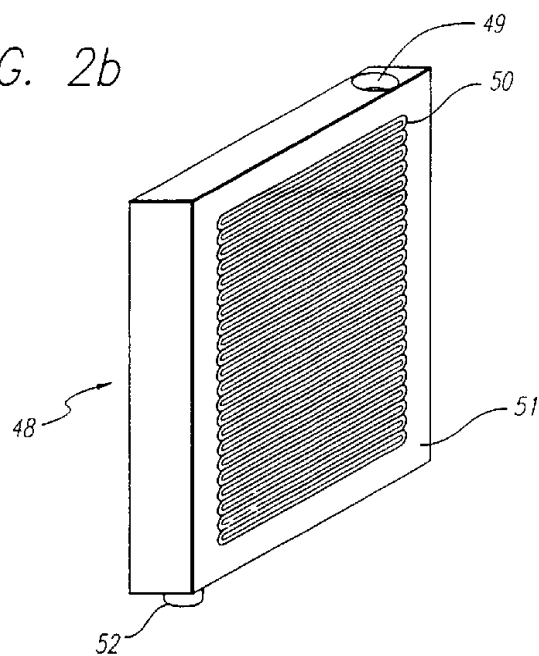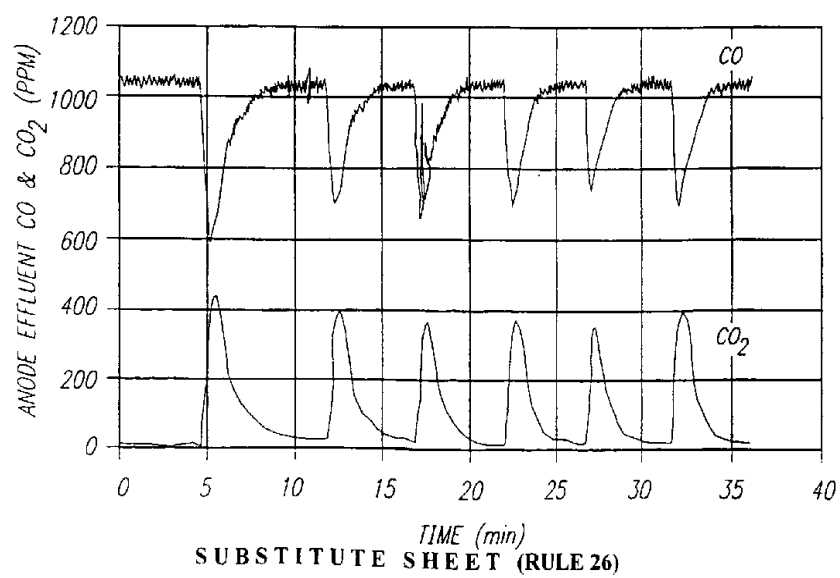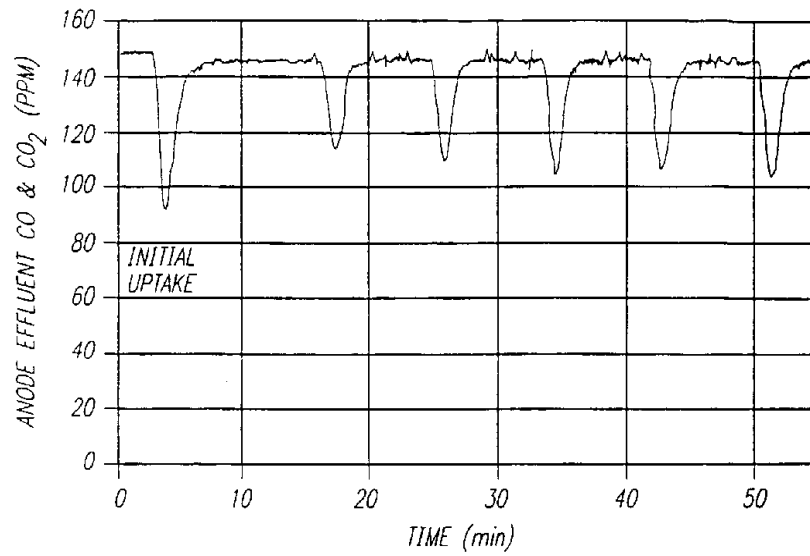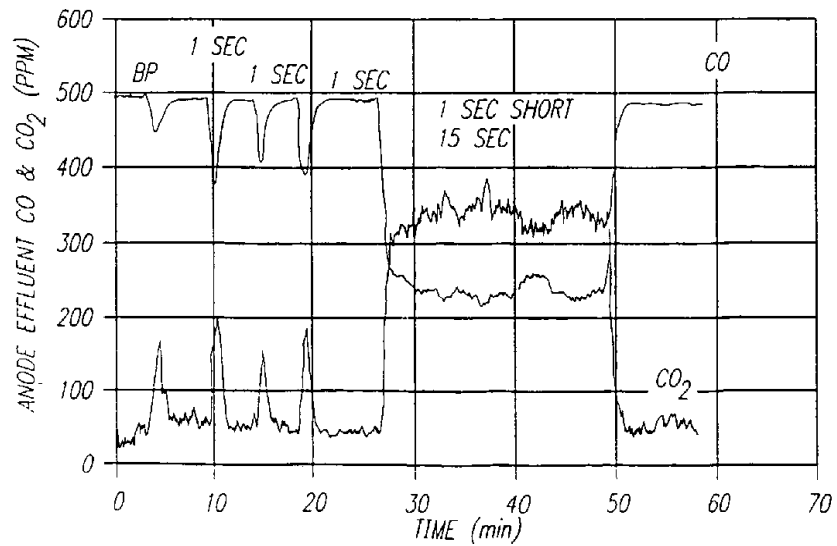of BALDWIN SHELSTON WATERS

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FIG. 1

FIG. 2a
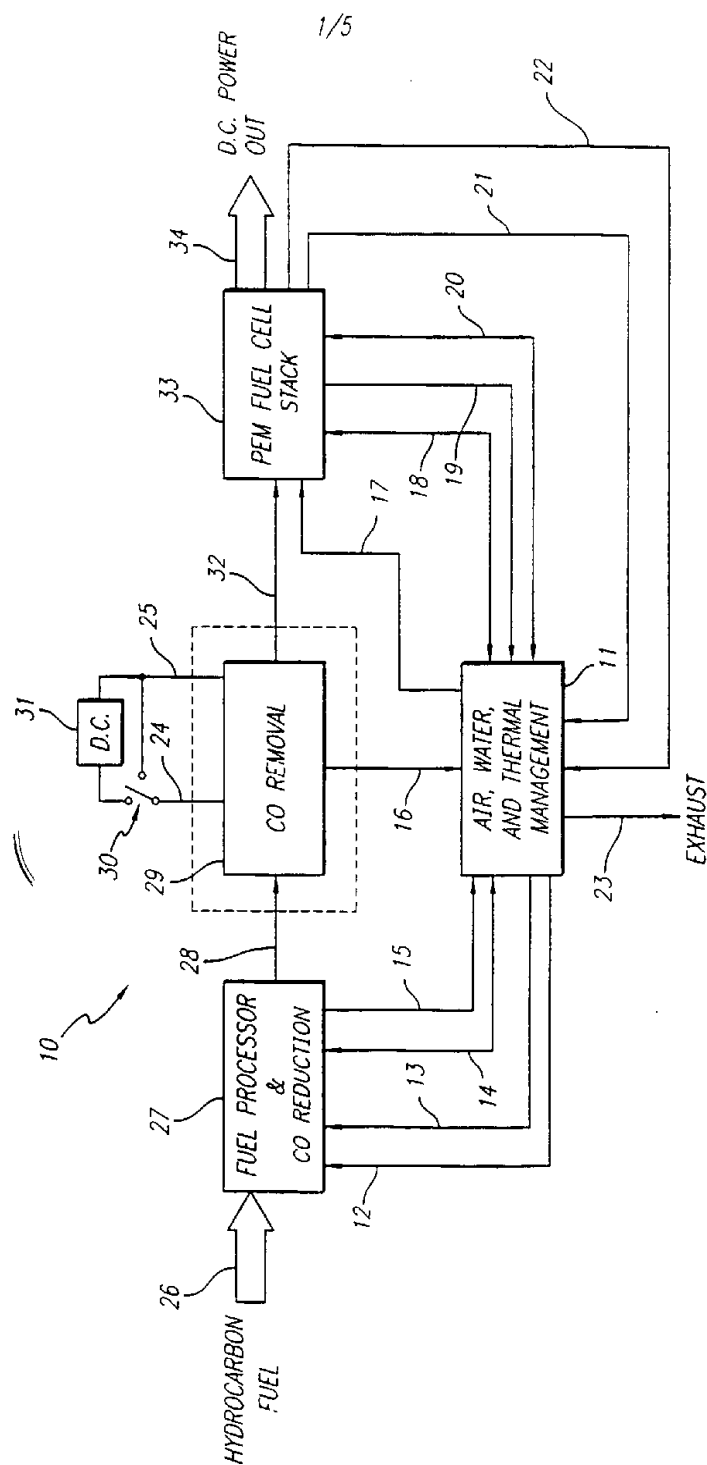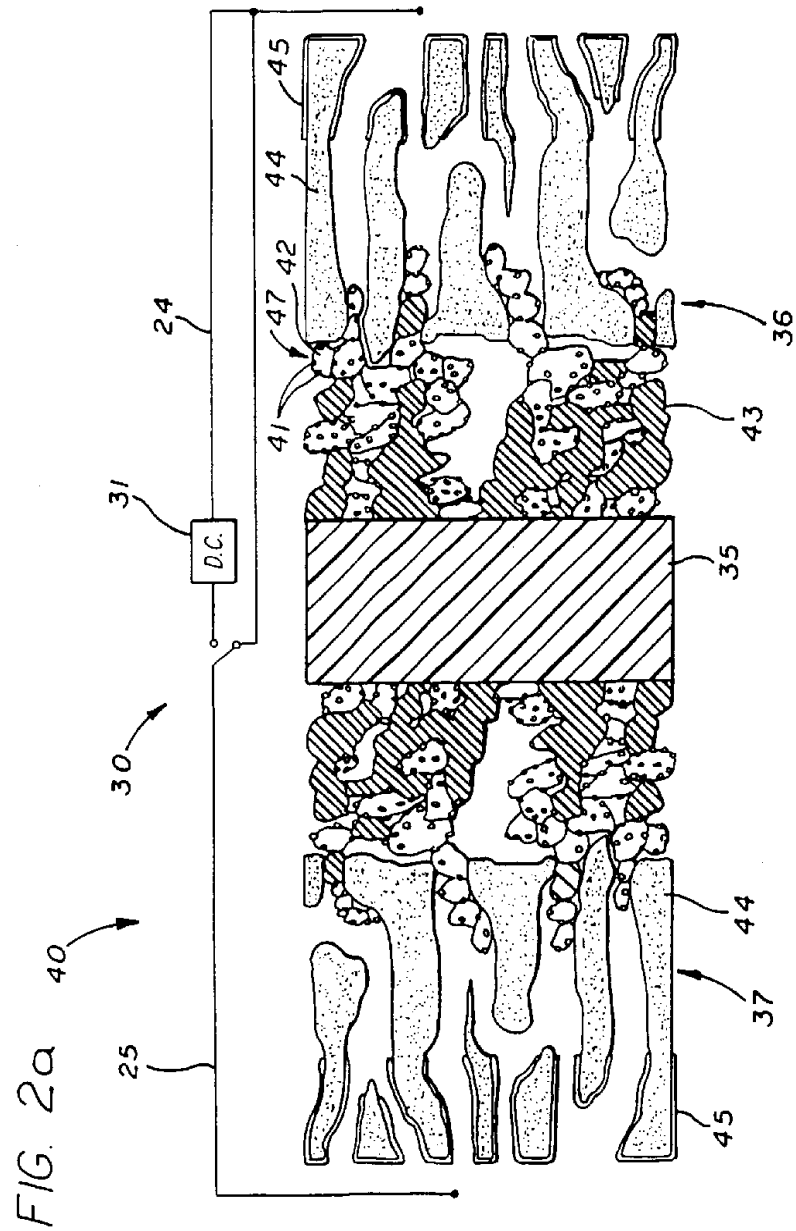
FIG. 2b

FIG. 3

FIG. 4

FIG. 5

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FIG. 6