An exhaust gas emitted from an engine (10) that contains nitrogen oxides is supplied to the cathode of a fuel cell (20), and a hydrogen-rich gas generated by the hydrogen gas generator (30) is supplied to the anode of the fuel cell (20). In the fuel cell (20), the nitrogen oxides are decomposed and electricity are generated by an electrochemical reaction between hydrogen and the nitrogen oxides. A hydrogen-separation membrane fuel cell, which operates at a temperature that is substantially the same temperature as that of the exhaust gas emitted from the engine (10) is used as the fuel cell (20).
EXHAUST GAS PURIFICATION SYSTEM AND METHOD FOR PURIFYING EXHAUST GAS

BACKGROUND OF THE INVENTION

[0001] Field of the Invention

The present invention relates to a system and a method for purifying exhaust gas, emitted from an internal combustion engine, that contains nitrogen oxides.

[0002] Description of the Related Art

Internal combustion engines are used as the driving power source for mobile conveyances such as vehicles. Typically, such internal combustion engines combust fuel and emit exhaust gases. These exhaust gases contain nitrogen oxides (NOx). Because nitrogen oxides pollute the atmosphere, they are usually removed by adsorption using an adsorbent or decomposed using a catalyst such as a NOx storage reduction catalyst or using plasma irradiation.


[0006] The process described in JP-A-2001-70748 may be applied to a mobile conveyance, such as a vehicle, that uses an internal combustion engine as a driving power source. However, the operating temperature of a molten carbonate fuel cell is extremely high, generally in the range of 600 to 700°C. Therefore, if the process described in JP-A-2001-70748 is applied to a vehicle using an internal combustion engine as a driving power source, it is necessary to preheat the exhaust gas of the internal combustion engine up to near the operating temperature of the molten carbonate fuel cell, thereby additionally requiring a preheating device to preheat the exhaust gas of the internal combustion engine. It leads to a reduction in the energy efficiency of a system having the internal combustion engine, and an increase in the size of the system.

SUMMARY OF THE INVENTION

[0007] The present invention provides a system and a method for purifying exhaust gas, emitted from an internal combustion engine, that contains nitrogen oxides, without reducing the energy efficiency or increasing the size of the system.

[0008] A first aspect of the present invention relates to an exhaust gas purifying system for purifying an exhaust gas, emitted from an internal combustion engine, that contains nitrogen oxides. The exhaust gas purifying system according to the first aspect has a fuel cell operating within a prescribed temperature range that includes the temperature of the exhaust gas. The fuel cell generates electricity by an electrochemical reaction between a prescribed fuel gas and nitrogen oxides contained in the exhaust gas.

[0009] In the first aspect of the present invention, the fuel cell uses the nitrogen oxides contained in the exhaust gas as an oxidant gas and uses hydrogen as the fuel gas to generate electricity by an electrochemical reaction between the hydrogen and the nitrogen oxides. In doing this, the anode reaction of the fuel cell may be expressed as $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$, and the cathode reaction may be expressed as $(2/X)\text{NO} + 2\text{H}^+ + 2\text{e}^- \rightarrow (1/X)\text{N}_2 + \text{H}_2\text{O}$. The nitrogen oxides are decomposed by a reaction expressed as $2\text{NO} + X\text{H}_2 \rightarrow N_2 + X\text{H}_2\text{O}$. According to the first aspect, because the fuel cell operates in a prescribed temperature range that includes the temperature of the exhaust gas, it is possible to supply the exhaust gas to the cathode of the fuel cell without preheating the exhaust gas. It is therefore not necessary to provide the exhaust gas purifying system with a preheating device to preheat the exhaust gas, thereby increasing energy efficiency and enabling compactness of the system. That is, the first aspect of the present invention enables to provide the purification of exhaust gas, emitted from an internal combustion engine, that contains nitrogen oxides without reducing energy efficiency or increasing size of the system.

[0010] In the first aspect of the present invention, the electrochemical reaction also decomposes the nitrogen oxides.

[0011] In the first aspect of the present invention, the fuel cell includes an electrolyte membrane in which a hydrogen-permeable metal layer that selectively allows hydrogen to permeate and an electrolyte layer having a proton-conductivity are laminated. That is, a hydrogen-separation membrane fuel cell is applied as the fuel cell. Because the operating temperature of the hydrogen-separation membrane fuel cell is approximately 400°C, which is approximately the same temperature as that of exhaust gas from a general internal combustion engine, the hydrogen-separation membrane fuel cell may be applied suitably to the present invention. Also, because the electrolyte membrane of the hydrogen-separation membrane fuel cell has a hydrogen-permeable metal layer with a relatively high strength, it is possible to make the electrolyte layer having the proton-conductivity thin, while maintaining the strength of the electrolyte membrane. Therefore, it is possible to make the membrane resistance of the electrolyte layer relatively low. As a result, by applying a hydrogen-separation membrane fuel cell to the present invention, it is possible to generate electricity while decomposing nitrogen oxides efficiently.

[0012] A noble metal such as palladium (Pd) or a palladium alloy, or a group 5 element, such as vanadium (V), niobium (Nb), tantalum (Ta) or the like may be used as the hydrogen-permeable metal layer. Various electrolytes, for example, a solid oxide, such as SrCeO$_3$ or BaCeO$_3$-based ceramic or the like, may be used as the electrolyte layer.

[0013] In the first aspect of the present invention, the cathode of the fuel cell has a platinum-based catalyst to promote the electrochemical reaction. Here, the term “platinum-based catalyst” includes, for example, platinum and alloys of platinum with ruthenium. By using a platinum-based catalyst as the cathode of the fuel cell, the fuel cell is capable of decomposing nitrogen oxides more efficiently as compared to a fuel cell using a cathode with other catalysts.

[0014] The first aspect of the present invention further includes a secondary battery storing electrical energy generated by the fuel cell. This enables to use the electrical energy generated by the fuel cell according to need while storing the electrical energy in the secondary cell temporarily.

[0015] A second aspect of the present invention relates to a method for purifying exhaust gas having the above-described elements as an exhaust gas purifying system. The present invention may be configured as a mobile conveyance in which the above-described exhaust gas purifying system is installed. Also, the various additional elements described above may be applied to each aspect of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] The foregoing and further objects, features, and advantages of the invention will become apparent from the
following description of example embodiments with reference to the accompanying drawings, wherein like numerals are used to represent like elements, and wherein:

[0017] FIG. 1 is a diagram showing a schematic view of an exhaust gas purifying system 100 according to one example embodiment of the present invention; and

[0018] FIG. 2 is a diagram showing a schematic view of a fuel cell 20.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0019] In the following description and the accompanying drawings, the present invention will be described in the order of an exhaust gas purifying system, a fuel cell, and variations, in more detail in terms of example embodiments.

[0020] FIG. 1 is a diagram showing a schematic view of the exhaust gas purifying system 100 according to one example embodiment of the present invention. The exhaust gas purifying system 100 is installed in a vehicle that uses an internal combustion engine as a driving power source.

[0021] As shown in FIG. 1, the exhaust gas purifying system 100 has an engine 10, a fuel cell 20, a hydrogen gas generator 30, and a battery 40.

[0022] The engine 10 combusts gasoline supplied from a gasoline tank (not shown), and emits exhaust gas. The temperature of the exhaust gas is approximately 400°C. The exhaust gas contains nitrogen oxides (NOx). These nitrogen oxides, as described below, are decomposed electrochemically by the fuel cell 20.

[0023] The hydrogen gas generator 30 as a hydrogen-supplying source uses gasoline, water, and air (oxygen) to perform reforming reactions and shift reactions and the like, and generates a hydrogen-rich gas. The reforming reactions of gasoline, which is a mixture of hydrocarbons, are expressed by equations (1) and (2). In these reforming reactions, hydrogen and carbon monoxide are generated by a reaction between gasoline and water vapor, and a reaction between gasoline and oxygen. In addition, the shift reaction oxidizes the carbon monoxide that is generated by the reforming reaction while using water vapor, and generates hydrogen. The shift reaction is expressed by equation (3). In the shift reaction, hydrogen and carbon dioxide are generated. The temperature of the hydrogen-rich gas generated by the hydrogen gas generator 30 is approximately 400°C.

\[
\begin{align*}
C_8H_{16} + nH_2O & \rightarrow nCO + (n+m/2)H_2 \\
C_8H_{16} + mO_2 & \rightarrow CO + mH_2 \\
CO + H_2O & \rightarrow CO_2 + H_2
\end{align*}
\]

[0024] The fuel cell 20 in this embodiment, as described below, has an electrolyte membrane in which a hydrogen-permeable metal layer that selectively allows hydrogen to permeate and an electrolyte layer having proton-conductivity are laminated. That is, the fuel cell 20 is a hydrogen-separation membrane fuel cell. The fuel cell 20 generates electricity by an electrochemical reaction between the fuel gas supplied to the anode and the oxidant gas supplied to the cathode. The operating temperature of the hydrogen-separation membrane fuel cell is approximately 400°C. The configuration of the fuel cell 20 is described in detail below.

[0025] The exhaust gas, emitted from the engine 10, that contains nitrogen oxides is supplied to the cathode of the fuel cell 20 through the pipe 52. The nitrogen oxides contained in the exhaust gas are used as the oxidant gas. The cathode off-gas discharged from the cathode of the fuel cell 20 is exhausted to the outside through the pipe 54.

[0026] The hydrogen-rich gas generated by the hydrogen gas generator 30 is supplied to the anode of the fuel cell 20 through the pipe 56. The hydrogen contained in the hydrogen-rich gas is used as the fuel gas. The anode off-gas discharged from the anode of the fuel cell 20 is exhausted to the outside through the pipe 58. The hydrogen contained in the anode off-gas, which has not been consumed in the electrical generation, may be recirculated to the pipe 56.

[0027] At the anode and cathode of the fuel cell 20, the reactions expressed by equations (4) and (5) generate electricity. When this electrical generation occurs, a reaction expressed by equation (6) electrochemically decomposes nitrogen oxides (NOx) into nitrogen and water. This enables to generate electricity while the exhaust gas containing nitrogen oxides is purified by the fuel cell 20.

Anode: \( H_2 \rightarrow 2H^+ + 2e^- \)  
Cathode: \( 2XNO\_x + 2H^+ + 2e^- \rightarrow H_2O + XN_2 \)  
\( 2NO_2 + H_2 \rightarrow N_2 + H_2O \)

[0028] The battery 40 temporarily stores the electrical energy generated by the fuel cell 20. By doing this, it is possible to use the electrical energy stored in the battery 40 according to need.

[0029] FIG. 2 is a diagram showing a schematic view of the fuel cell 20. Here, the cross-sectional structure of a unit cell 200 composing the fuel cell 20 is shown schematically. The unit cell 200 is formed by sandwiching in a membrane electrode assembly 210 (hereinafter referred to as “MEA”) between separators 220.

[0030] The separators 220, as shown in FIG. 2, have concavoconvex shapes to form flow paths that flow hydrogen as a fuel gas into the anode side of theMEA 210 and the exhaust gas from the engine 10 as the oxidant gas into the cathode side of the MEA 210, respectively. Various materials having electrical conductivity, such as carbon or metal and the like, may be applied as the materials of the separator 220.

[0031] The MEA 210 is configured in such a manner that hydrogen-permeable metal layer 212 that selectively allowing hydrogen to permeate, an electrolyte layer 214 having a proton-conductivity, and the cathode 216, are laminated in that order. The hydrogen-permeable metal layer 212 also functions as the anode. Each of these layers may be formed by various methods such as, for example, physical vapor deposition.

[0032] In this embodiment, a palladium film is used as the hydrogen-permeable metal layer 212. A Perovskite solid electrolyte is used as the electrolyte layer 214. Platinum having a catalytic ability to promote the electrochemical reaction is used as the cathode 216. These materials and film thicknesses may be arbitrarily selected and set.

[0033] The fuel cell 20 in this embodiment, as described above, is a hydrogen-separation membrane fuel cell, in which the MEA 210 has a hydrogen-permeable metal layer 212 with a relatively high strength. Therefore, it is possible to make the electrolyte layer 214 having a proton-conductivity relatively thin, while maintaining the strength of the MEA 210. Thus, it is possible to make the membrane resistance of the electrolyte layer 214 relatively low. Consequently, by using a hydrogen-separation membrane fuel cell, it is possible to generate electricity while decomposing nitrogen oxides efficiently.
According to the exhaust gas purifying system 100 described above, the fuel cell 20 uses nitrogen oxides contained in exhaust gas from the engine 10 as an oxidant gas and hydrogen as a fuel gas to generate electricity by an electrochemical reaction between the hydrogen and the nitrogen oxides. Here, the nitrogen oxides are decomposed by the electrochemical reaction expressed by the equation (10).

Because a hydrogen-separation membrane fuel cell as the fuel cell 20 operates at a temperature that is substantially the same temperature as that of the exhaust gas from the engine 10, the exhaust gas may be supplied to the cathode of the fuel cell 20 without preheating the exhaust gas. Therefore, it is not necessary to provide the exhaust gas purifying system 100 with a preheating device for preheating the exhaust gas from the engine 10, thereby enabling a system with increased energy efficiency and compactness. That is, according to the exhaust gas purifying system 100 of this embodiment, the exhaust gas containing nitrogen oxides may be purified without reducing the energy efficiency or increasing the size of the system.

While the present invention has been described with reference to the embodiment thereof, the present invention is not limited to the described embodiment. Various example embodiments may be applied to the present invention within the scope and spirit thereof. For example, variations are described below.

While the hydrogen-rich gas generated by the hydrogen gas generator 30 has been supplied to the anode of the fuel cell 20 in the above embodiment, the present invention is not limited to this. For example, a hydrogen tank as the hydrogen-supplying source may be provided in place of the hydrogen gas generator 30.

While the battery 40 has been provided in the exhaust gas purifying system 100 in the above embodiment, the battery 40 may not be provided in the exhaust gas purifying system 100. Here, the electrical energy generated by the fuel cell 20 may be used serially.

While platinum has been used as the cathode 216 in the above embodiment, the present invention is not limited to this. However, by using a platinum-based catalyst as the cathode 216, it is possible to generate electricity and decompose nitrogen oxides more efficiently as compared to other catalysts.

While the fuel cell 20, that is, a hydrogen-separation membrane fuel cell operating at approximately 400° C. has been used because the temperature of the exhaust gas from the engine 10 is approximately 400° C., the present invention is not limited to this. A fuel cell operating within a prescribed temperature range that includes the general temperature of the exhaust gas from an internal combustion engine may be used.

While the invention has been described with reference to example embodiments thereof, it is to be understood that the invention is not limited to the described embodiments or constructions. To the contrary, the invention is intended to cover various modifications and equivalent arrangements. In addition, while the various elements of the example embodiments are shown in various combinations and configurations, other combinations and configurations, including more, fewer, or only a single element, are also within the spirit and scope of the invention.

1. - 7. (canceled)
8. An exhaust gas purifying system comprising:
   - an internal combustion engine that combusts gasoline and emits an exhaust gas that contains nitrogen oxides;
   - a hydrogen-supplying source that supplies a hydrogen-rich gas; and
   - a fuel cell that is supplied with the exhaust gas and the hydrogen-rich gas, wherein the fuel cell operates within a prescribed temperature range that includes the temperature of the exhaust gas and generates electricity by an electrochemical reaction between hydrogen contained in the hydrogen-rich gas and the nitrogen oxides contained in the exhaust gas,
   wherein the fuel cell comprises an electrolyte membrane in which a hydrogen-permeable metal layer that selectively allows the hydrogen to permeate and an electrolyte layer having a proton-conductivity are laminated.

9. The exhaust gas purifying system according to claim 8, wherein the electrochemical reaction also decomposes the nitrogen oxides.
10. The exhaust gas purifying system according to claim 8, wherein a cathode of the fuel cell has a catalytic layer that promotes the electrochemical reaction.
11. The exhaust gas purifying system according to claim 8, further comprising a secondary battery that stores the electricity generated by the fuel cell.
12. A method for purifying exhaust gas emitted from an internal combustion engine that contains nitrogen oxides, comprising:
   providing a fuel cell that operates within a prescribed temperature range including the temperature of the exhaust gas and generates electricity by an electrochemical reaction between hydrogen contained in a prescribed fuel gas and the nitrogen oxides contained in the exhaust gas,
   wherein the fuel cell comprises an electrolyte membrane in which a hydrogen-permeable metal layer that selectively allows the hydrogen to permeate and an electrolyte layer having a proton-conductivity are laminated;
   supplying the prescribed fuel gas to an anode of the fuel cell and the exhaust gas to a cathode of the fuel cell; and decomposing the nitrogen oxides along with generating electricity by the electrochemical reaction.
13. The exhaust gas purifying system according to claim 9, wherein a cathode of the fuel cell has a catalytic layer that promotes the electrochemical reaction.
14. The exhaust gas purifying system according to claim 9, further comprising a secondary battery that stores the electricity generated by the fuel cell.
15. The exhaust gas purifying system according to claim 10, further comprising a secondary battery that stores the electricity generated by the fuel cell.

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