

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
27 July 2006 (27.07.2006)

PCT

(10) International Publication Number
WO 2006/077461 A2(51) International Patent Classification:
H01M 8/04 (2006.01) *H01M 4/92* (2006.01)(21) International Application Number:
PCT/IB2005/003387(22) International Filing Date:
12 November 2005 (12.11.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2004-329615 12 November 2004 (12.11.2004) JP
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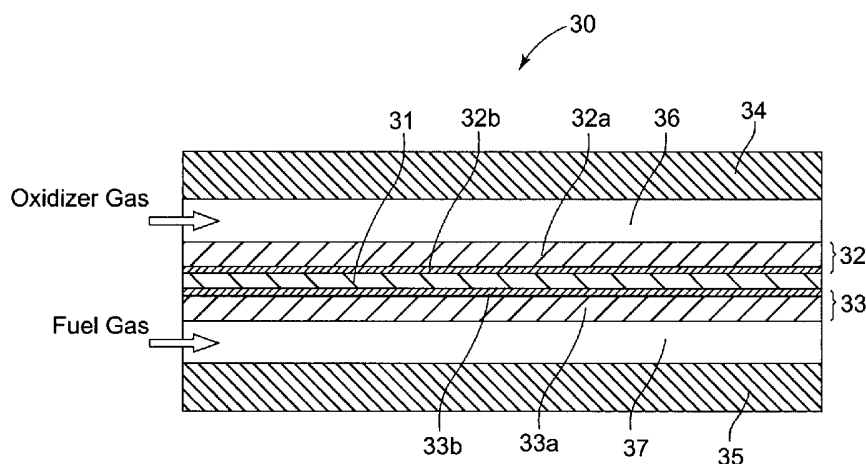
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(US).(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG,
KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY,
MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO,
NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK,
SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VC, VN, YU, ZA, ZM, ZW.(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT,
RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished
upon receipt of that report

[Continued on next page]

(54) Title: FUEL CELL SYSTEMS AND CONTROL METHODS



(57) Abstract: The disclosure relates to fuel cell systems and methods for improving the operating efficiency and lifetime of fuel cells. In one aspect, the disclosure provides fuel cell systems including a fuel cell containing a fuel electrode, an oxidizer electrode, an electrolyte film between the fuel electrode and the oxidizer electrode, and a first catalyst layer including a first reversibly oxidized catalyst surface on a first catalyst support situated between the electrolyte film and the oxidizer electrode. In certain embodiments, the fuel cell system includes a second catalyst layer including a second reversibly oxidized catalyst surface on a second catalyst support situated between the electrolyte film and the fuel electrode. The disclosure also provides methods for operating a fuel cell in which an active catalyst surface is reversibly oxidized at the time of starting-up, shutting-down or altering the power output of the fuel cell by applying a voltage to the electrodes from a secondary energy storage cell such as a battery. The method may reduce irreversible degradation of a catalyst layer during fuel cell start-up, thereby improving fuel cell cycle stability and lifetime.



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FUEL CELL SYSTEM AND CONTROL METHOD

TECHNICAL FIELD

[0001] The invention relates to fuel cell systems and methods for improving the operating efficiency and lifetime of fuel cells.

BACKGROUND

[0002] Conventional fuel cell systems contain one or more fuel cells including electrodes, generally an anode and a cathode coated with a platinum type metal catalyst, an electrolyte between the anode and the cathode, and a separator board with a gas passage formed to supply oxidizer gas (e.g. air) to the cathode, and fuel gas (e.g. hydrogen) to the anode. When the fuel cell stops generating power, the cathode potential is generally adjusted to a pre-determined voltage lower than the standard hydrogen electrode potential to avoid electrolysis of water and consequential generation of hydrogen and oxygen gas at the cathode.

[0003] During fuel cell shutdown, however, the atmospheric oxygen concentration at the oxidizer electrode (cathode) also needs to be reduced to as low a level as possible, preferably close to 0% (by volume), in order to keep the potential at the oxidizer electrode from 0.6 V to 0.8 V. Even if the oxidation electrode is effectively blanketed with a nitrogen atmosphere created by consuming the oxygen in the air before shutdown, oxygen may diffuse into proximity with the cathode as time elapses, oxidizing the catalyst and causing deterioration of the fuel cell power output performance over many start-up and shutdown cycles.

[0004] During fuel cell start-up, oxidizer gas (such as air) exists at the oxidizer electrode, and both oxidizer gas rich regions and fuel gas (such as hydrogen) rich areas may be formed at the fuel electrode (anode). For example, if the system is started up from an air-mixed condition at both the fuel and oxidizer electrodes, hydrogen-rich regions may be formed in the fuel gas passage while other regions may not contain any hydrogen. This is particularly likely at the beginning stage of cell start-up immediately after starting hydrogen flow to the fuel gas passage at the fuel electrode. In the hydrogen rich regions near the fuel electrode, the same reaction as

regular fuel cell operating condition occurs, and a high electric potential of more than 1 V is produced at the oxidizer electrode.

[0005] On the other hand, in the area without hydrogen at the fuel electrode, the following reaction may occur if water is present at the corresponding oxidizer electrode:



[0006] In the air rich regions at the fuel electrode, the following reaction may occur, producing water:



The water produced by the reaction of equation 2 acts to autocatalytically increase the rate of the reaction of equation 1. As a result, the carbon carrier which supports the oxidation catalyst (such as Pt) may oxidize, corrode or otherwise irreversibly degrade, and the catalytic activity of the platinum catalyst at the oxidizer electrode may be greatly deteriorated, thereby causing performance deterioration of the power generation ability of fuel cell over many start-up and shutdown cycles.

[0007] Among the art pertaining to conventional fuel cell systems, published U.S. Patent Application, No. 2002/0076582 describes a method to supply hydrogen to the electrodes so that the boundary between hydrogen-containing and non-hydrogen-containing areas ("hydrogen/air front" hereafter) can travel through the fuel gas passage in a short time (less than one second). In the above-mentioned art, however, some measures are required to provide a driving force for the hydrogen/air front to travel through the fuel cell passage in such a short time (depending on the fuel gas passage design of the fuel cell). For example, one measure is to place additional equipment such as a compressor in the middle of the piping passage that supplies hydrogen to fuel electrode gas passage. Another measure is to make the cross section area of the fuel gas passage smaller so that the fuel gas flows faster. In the former case, there is a problem that the fuel cell system becomes bigger. In the latter case, there is a problem that the reaction efficiency is remarkably lowered because of the smaller reaction surface.

[0008] The art continues to search for fuel cell systems and methods of operating fuel cells to improve the long term cycling performance and lifetime of fuel cells.

SUMMARY

[0009] In general, the invention relates to fuel cell systems and methods for improving the operating efficiency and lifetime of fuel cells. The methods generally include forming an oxidized film on the surface of an active catalyst within a catalyst layer included as a component in a fuel cell electrode during fuel cell shutdown. The oxidized film reversibly decreases the catalytic activity of the catalyst layer, thereby reducing the likelihood of irreversible oxidation reactions at the fuel and oxidizer electrodes during fuel cell start-up, when both hydrogen and air exist at the fuel electrode. Consequently, the power output efficiency and lifetime of the fuel cells may be maintained at a high level.

[0010] In one embodiment, a fuel cell system includes a fuel cell containing a fuel electrode, an oxidizer electrode, an electrolyte film between the fuel electrode and the oxidizer electrode, and a first catalyst layer including a catalyst having a first reversibly oxidized catalyst surface on a first catalyst support situated between the electrolyte film and the oxidizer electrode. In certain embodiments, the fuel cell system may also include a second catalyst layer including a second catalyst having a second reversibly oxidized catalyst surface on a second catalyst support situated between the electrolyte film and the fuel electrode.

[0011] In another embodiment, a method includes operating a fuel cell in which the active catalyst surface is reversibly oxidized at the time of starting-up or shutting-down the fuel cell by applying a voltage to the electrodes from a secondary energy storage cell such as a battery. The method may reduce irreversible degradation of the catalyst layer during fuel cell start-up, thereby improving fuel cell cycling stability and lifetime.

[0012] The details of one or more embodiments of the invention are set forth in the accompanying drawings and the description below. Other features, objects, and advantages of the invention will be apparent from the description and drawings, and from the claims.

BRIEF DESCRIPTION OF DRAWINGS

- [0013] Figure 1 illustrates a schematic cross-sectional drawing of a unit fuel cell assembly of an exemplary fuel cell system.
- [0014] Figure 2 illustrates a schematic cross-sectional drawing of the unit fuel cell assembly under operating conditions wherein air is allowed into proximity of the fuel electrode.
- [0015] Figure 3 illustrates a schematic drawing of a fuel cell control system operating in fuel cell start-up mode according to one embodiment of the present invention.
- [0016] Figure 4 illustrates a flowchart showing a sequence of steps used by the fuel cell control system of Fig. 3 when starting-up the fuel cell system according to another embodiment of the present invention.
- [0017] Figure 5a illustrates a magnified view of an exemplary fuel electrode catalyst layer before application of a voltage to the fuel cell electrode stack.
- [0018] Figure 5b illustrates a magnified view of an exemplary fuel electrode catalyst layer after application of a voltage to the fuel cell electrode stack.
- [0019] Figure 6 illustrates a graph showing the time-wise variation in fuel cell output voltage before and after application of an external voltage to the fuel cell electrode stack according to another embodiment of the present invention.
- [0020] Figure 7 illustrates a flowchart showing a sequence of steps used by the fuel cell control system of Fig. 3 when shutting-down the fuel cell system according to another embodiment of the present invention.
- [0021] Figure 8 illustrates a graph showing fuel cell voltage characteristics as a function of current density for an exemplary unit fuel cell.
- [0022] Figure 9 illustrates a schematic drawing of a fuel cell control system operating in fuel cell shutdown mode according to another embodiment of the present invention.
- [0023] Figure 10 illustrates a flowchart showing a sequence of steps used by the fuel cell control system of Fig. 9 when shutting-down the fuel cell system according to another embodiment of the present invention.
- [0024] Figure 11 illustrates another flowchart showing a sequence of steps used by the fuel cell control system of Fig. 9 when a voltage detection means detects a high voltage operating condition of a fuel cell stack and applies a second predetermined voltage to the electrodes within the fuel cell stack to modulate the high voltage operating condition.

[0025] Figure 12 illustrates a graph showing the time-wise variation in fuel cell output voltage illustrating the high voltage operating condition before application of a predetermined voltage to the electrodes within the fuel cell stack, and the lower operating voltage obtained after applying the predetermined voltage, according to another embodiment of the present invention.

[0026] Figure 13 illustrates a graph showing the relationship between the predetermined voltage and the change in unit fuel cell operating voltage per 1,000 cycles resulting from the applied predetermined voltage for the embodiment illustrated in Figures 11 and 12.

[0027] Figure 14 illustrates another flowchart showing a sequence of steps used by the fuel cell control system of Fig. 9 when a voltage detection means detects a voltage operating condition of a fuel cell stack above a second predetermined voltage but below a third predetermined voltage, and applies a predetermined voltage to the electrodes within the fuel cell stack to effect a reduction in fuel cell stack output power.

[0028] Figure 15 illustrates a graph showing cyclic voltammogram in which the current density of the fuel cell is plotted as a function of the reversible hydrogen fuel cell electrode potential as the potential applied to the fuel electrode and oxidizer electrode within the unit fuel cell was increased from 0.04 volts to 0.9 volts while supplying hydrogen fuel gas to the fuel electrode, and nitrogen to the oxidizer electrode.

DETAILED DESCRIPTION

[0029] In various embodiments, this invention is directed at solving many of the problems with conventional fuel cells systems, particularly with methods of start-up or shutting-down fuel cell systems. In some embodiments, the invention is directed at simple and effective control of the fuel cell start-up and shutdown procedures to avoid or minimize the effects of undesirable chemical reactions at the oxidizer electrode during start-up, reactions which irreversibly degrade the power output and lifetime of the fuel cell system.

[0030] In some embodiments of the invention, a fuel cell system with a fuel cell consists of a fuel electrode, an oxidizer electrode and an electrolyte film between them, as well as a catalyst layer (which holds a redox catalyst) between the electrolyte film and each of the electrodes. The fuel cell system performs an oxidized film producing process in which the catalyst surface is oxidized at the time of starting-up or shutting-down of the said fuel cell so that the oxidized film decreases the catalyst activity.

[0031] In one embodiment of the invention, an oxidized film is formed on the surface of the catalyst layer of the fuel cell cathode at the time of cell start-up or shutdown, for example, so that the catalyst activity is reversibly decreased. This prevents oxidizer electrode (cathode) deterioration that may occur when both hydrogen and air exist at the fuel electrode (anode), for example, under start-up conditions wherein hydrogen is supplied to the fuel electrode and air is in the proximity of the fuel electrode.

[0032] Figure 1 illustrates a schematic cross-sectional drawing of a unit fuel cell 30 of an exemplary fuel cell system. One or more unit fuel cells 30 may be used to form a fuel cell stack 1 (Fig. 3), which is used in a first mode for carrying out of this invention. The unit fuel cell 30 includes a selectively permeable polymer electrolyte film 31 that exhibits good proton conductivity and permeability, as well as an oxidizer electrode (cathode) layer 32 and a fuel electrode (anode) layer 33 surrounding the electrolyte film 31. The unit fuel cell 30 also includes an oxidizer gas separator 34, and a fuel gas separator 35 located outside of the unit fuel cell 30.

[0033] The oxidizer electrode layer 32 and the fuel electrode layer 33 have gas diffusion layers 32a and 33a, and may include a porous plate material underlaying catalyst layers 32b and 33b, which may include a redox catalyst on a catalyst support. There is also an oxidizer gas passage 36 between the oxidizer electrode layer 32 and the oxidizer gas separator 34. Furthermore, there is a fuel gas passage 37 between the fuel electrode layer 33 and the fuel gas separator 35. The oxidizer gas passage 36 and the fuel gas passage 37 are constructed so that the oxidizer gas passing into the fuel cell through the oxidizer gas passage 36, and the fuel gas passing into the fuel cell through the fuel gas passage 37, flow in about the same direction.

[0034] As noted above, the unit fuel cell 30 includes a selectively permeable polymer electrolyte film 31 that exhibits good proton conductivity and permeability. One suitable selectively permeable electrolyte film 31 is a Nafion™ membrane (DuPont Corp., Wilmington, Delaware). In addition, the oxidizer electrode layer 32 and the fuel electrode layer 33 may include a porous plate material which may include a woven or non-woven carbon fiber structure, and catalyst layers 32b and 33b, which include a redox catalyst on a catalyst support. Suitable redox catalysts include metals or metal alloys including one or more of platinum, palladium and rhenium. Suitable catalyst supports include carbon or mixtures of carbon and other materials, preferably in particulate form.

[0035] Figure 2 illustrates a schematic cross-sectional drawing of the unit fuel cell 30 under operating conditions wherein air is allowed into proximity of the fuel electrode.

Air is generally used as the oxidizer gas supplied to the oxidizer gas passage 36, while hydrogen gas is generally used as the fuel gas. The following chemical reactions occur at the fuel electrode and the oxidizer electrode, respectively, within the unit fuel cell 30 during regular operation:

At Fuel Electrode: $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ (Equation 3), and

At Oxidizer Electrode: $2\text{H}^+ + 1/2 \text{O}_2 + 2\text{e}^- \rightarrow \text{H}_2\text{O}$. (Equation 4).

[0036] At the fuel electrode, hydrogen in the fuel gas is decomposed into proton and electron, as shown in Equation 3. The protons diffuse through the electrolyte film 31, reaching the oxidizer electrode layer 32. The electrons flow into an external circuit (which is not shown in the figure), providing an electrical power output in the form of a direct current voltage. On the other hand, at the oxidizer electrode layer 32, the protons diffuse through the electrolyte film 31, electrons travel through the external circuit (which is not shown in the figure) and oxygen present in the air reacts at the interface of three phases, as shown in Equation 4.

[0037] When the fuel cell stack 1 (Fig. 3) is used as a power source of mobile equipment such as automobile, cycles of starting-up and shutting-down are repeated frequently. When operation of the fuel cell stack 1 is stopped, it is left without supplies of hydrogen or air within the fuel cell stack 1. When this condition continues for a prolonged period of time, it is possible that air may penetrate from outside and diffuse into the fuel gas passage 37. When the fuel cell system is started up from an air-rich condition in the fuel gas passage 37, a condition shown in Figure 2 occurs in the fuel cell stack 1 at the initial stage of the start-up.

[0038] Under the conditions shown in Figure 2, wherein air fills the oxidizer gas passage 36, both hydrogen gas-containing areas (area A) and air-containing areas (area C) may be formed in the fuel gas passage 37. Also, interface B, located between the area A and area C, is formed ("hydrogen/air front B" hereafter).

[0039] In the area A, reactions of Equations 3 and 4 occur during regular operation, producing a high electric potential of more than 1 V at the fuel electrode. On the other hand in the area C, beyond the hydrogen/air front B, the reaction of Equation 1 occurs at the oxidizer electrode layer 32, and the reaction of Equation 2 occurs at the fuel electrode layer 33. That causes oxidation, corrosion and irreversible deterioration of the carbon support of the catalyst layer 32b, which supports platinum to form the active catalytic

surface of the oxidizer electrode layer 32. The reaction of Equation 1 occurs only on the surface of the platinum where it meets carbon. This oxidation and corrosion of the carbon support degrades the oxidizer electrode layer 32, causing irreversible deterioration of the power output and efficiency of the fuel cell stack 1. Thus in certain embodiments, the present invention provides a fuel cell system which prevents such irreversible deterioration of the oxidizer electrode 32.

[0040] Figure 3 describes a fuel cell system according to a first embodiment of the disclosed invention. This embodiment illustrates a fuel cell stack 1, an air supply means (illustrated by a compressor) 2 which supplies air to the oxidizer gas passage 36, a hydrogen storage container 3 which supplies compressed hydrogen gas to the fuel gas passage 37, an optional load 4 which consumes a portion of the electric power generated by the fuel cell stack 1, (a voltage application means (illustrated by a secondary cell, e.g. a battery) 5, which stores a portion of the electric power generated by the fuel cell stack 1, and a voltage detection means (illustrated by a voltage sensor) 17 which detects application voltage by the battery 5.

[0041] An optional air filter 16, which removes impurities in the air, may be placed upstream of the compressor 2. The compressor 2 supplies air to the fuel cell stack 1. Emission gas (e.g. exhausted air) from the fuel cell stack 1, which contains unused oxygen, is supplied to a hydrogen consuming device 15 before venting to the ambient air.

[0042] Compressed hydrogen gas is supplied from the hydrogen storage container 3 via the fuel gas passage 37, decompressed using a decompression valve 6 in the hydrogen supply passage 9, and passed through a flow controller 7 to regulate the delivery rate of hydrogen to the fuel cell stack 1. Unused hydrogen gas from the fuel cell stack 1 is optionally directed to a hydrogen recirculation passage 10 by a recycle compressor 11, sent through a three-way valve 12 and the hydrogen supply passage 9, and re-supplied to the fuel cell stack 1.

[0043] A large volume of nitrogen gas from the air exiting the oxidizer electrode layer 32 through the electrolyte film 31 can be mixed with the hydrogen gas emissions from the fuel cell stack 1. Hydrogen emitted from the fuel cell stack 1 may then be introduced to the hydrogen emission passage 14, which is separated from the hydrogen recirculation passage 10 by another three-way valve 13, and then supplied to the hydrogen consuming device 15 to be consumed. The hydrogen consuming device 15 may contain hydrogen consuming catalysts, and emission gas from the oxidizer electrode side of the fuel cell stack 1 may be supplied to the hydrogen consuming device 15. This device consumes

hydrogen in the emission gas, and then emits hydrogen-free gas outside of the fuel cell system.

[0044] An optional electrical power load 4 is electrically connected to the oxidizer electrode board 20 and fuel electrode board 21 of the fuel cell stack 1, thereby consuming electric power generated by the fuel cell stack 1. Between the fuel cell stack 1 and the load 4, a Switch 22 is placed to engage or disengage (i.e. switch ON/OFF) the electrical connections between the fuel cell stack 1 and the load 4. A battery 5 is electrically connected in parallel to the fuel cell stack 1 and the load 4, electrically connecting the fuel cell stack 1 to the load 4, and stores a part of the electrical power (excess power) generated by the fuel cell stack 1. The battery 5 can also supply electric power to the fuel cell stack 1 and the load 4.

[0045] Figure 3 also illustrates a switch 23 adapted to engage or disengage (i.e. switch ON/OFF) the electric connections to the fuel cell stack 1 or the load 4. With both switches properly engages, the fuel cell stack 1, the load 4 and the Battery 5 can be electrically connected to or disconnected from one another. In addition, an optional electronic process controller 40 (e.g. a computer, microprocessor, programmable logic controller, and the like) is shown installed to control the compressor 2, the flow controller 7, the three-way valves 12 and 13, the recycle compressor 11 and the Switches 22 and 23.

[0046] The following figures illustrate exemplary embodiments within the scope of the invention. One skilled in the art understands that while the embodiments illustrated in the following figures and related written description describe catalyst layers including platinum as the active redox catalyst material, other catalytically active metals, for example palladium, rhenium and their combinations and equivalents, may be used alone or in combination with platinum with deviating from the disclosed invention.

[0047] Figure 4 illustrates a flowchart showing a sequence of steps used by the fuel cell control system of Fig. 3 when starting-up the fuel cell system according to another embodiment of the present invention. When the fuel cell system operation is stopped, both of the switches 22 and 23 are OFF. That is, the fuel cell stack 1, the load 4 and the battery 5 are not electrically connected one another. In addition, both the compressor 2 and the recycle compressor 11 are stopped.

[0048] When the electronic process controller 40 detects the start-up order of the fuel cell system, at Step S100, Switches 22 and 23 are turned ON, the battery 5 and the fuel cell stack 1 are electrically connected so as to have the oxidizer electrode as anode, and a predetermined voltage (the first predetermined voltage) V1 is applied to the fuel cell stack

1. If air is mixed in the fuel and oxidizer electrodes, the electric potential before application of the battery 5 may be 1.2 volts at both the fuel electrode and the oxidizer electrode of the unit fuel cell 30. Here, the electric potential under the condition where hydrogen exists at the fuel electrode is assumed to be 0 volts. When the predetermined voltage V1 is applied to the fuel cell stack 1, the electric potential at the catalyst layer 32b is increased to form an oxidized film on the platinum surface of the catalyst layer 32b. In this embodiment, the predetermined voltage V1 is indicated by the voltage that is applied to the unit fuel cell 30, that is, the voltage per unit cell 30. Hereinafter, the predetermined voltage refers to a voltage per unit fuel cell 30. Details of setting the predetermined voltage V1 are discussed later in this disclosure (note that Step S100 constitutes use of an oxidized film producing means).

[0049] During Step S100 a reversibly oxidized film may be formed on the surface of the platinum particles supported on the carbon support in the catalyst layer 32b of the oxidizer electrode (cathode) 32A reversibly oxidized film may also be formed on the surface of the platinum particles supported on the carbon support in the catalyst layer 33b of the fuel electrode (anode) 33. When the battery 5 applies an electrical potential to the fuel cell stack 1, the platinum of the catalyst particles may react as follows:

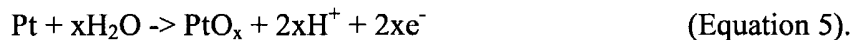


Figure 5 shows the change from the condition where there is no oxidized film formed on the surface of platinum, as shown in Figure 5(a), to the condition that oxidized film is formed on the surface of platinum, as shown in Figure 5(b). When the reversibly oxidized film is formed on the surface of the platinum, its catalytic activity is substantially degraded, and it may become catalytically inactive.

[0050] If the fuel cell system is started up from air-mixed condition at the fuel electrode, the reaction of Equation 1 occurs at the oxidizer electrode only on the surface of platinum where it meets carbon. When the oxidized film is formed on the surface of platinum, the catalyst activity is decreased so that the reaction of Equation 1 is suppressed. This may prevent oxidation, corrosion and irreversible deterioration of the carbon support.

[0051] At Step S101, controller 40 determines whether a predetermined time T1 has elapsed since the switches 22 and 23 were turned ON. If the predetermined time T1 has elapsed, the electronic process controller proceeds to Step S102. Here, the predetermined time T1 is selected such that the reaction of Equation 1 reaction is suppressed even if hydrogen is supplied to the fuel electrode at Step S103, and carbon oxidation or corrosion

reaction thus cannot occur. This predetermined time T1 depends on the catalyst material and/or the catalyst layer 32 and 33 materials. The longer the duration of T1, the more oxidized film is formed. But longer T1 also prolongs start-up time. Preferably, T1 is about 1 second, but T1 may generally be selected to be as short as about 0.1 seconds and as long as about 90 seconds.

[0052] At Step S102, controller 40 turns of the switch 23 to cease applying voltage from the battery 5 to the fuel cell stack 1.

[0053] At Step S103, controller 40 starts supplying hydrogen from the compressed hydrogen storage container 3 to the fuel electrode. When hydrogen is supplied to the fuel electrode, the hydrogen/air front B is formed at the fuel electrode as mentioned previously. However, oxidized film is already formed on the surface of platinum in the catalyst layer 32b at the oxidizer electrode, so that the catalytic activity of the platinum is degraded. That prevents the carbon oxidation and corrosion reaction (as shown in Equation 1) on the catalyst layer 32b at the fuel electrode. Then the hydrogen/air front B moves downstream as hydrogen supply arrives, where regular generating reactions of Equations (3) and (4) in the fuel cell stack 1.

[0054] At Step S104, controller 40 starts supplying air from the compressor 2 to the oxidizer electrode to start power generation as required by the fuel cell system.

[0055] By the above-mentioned controls, before starting the hydrogen supply, oxidized film is formed on the surface of the platinum catalyst in the catalyst layer 32b at the oxidizer electrode, and then hydrogen is supplied. Therefore the catalyst activity is decreased until the hydrogen/air front B is purged from the fuel electrode, so as to prevent deterioration by carbon oxidation and corrosion of the catalyst layer 32b during start-up of the fuel cell stack 1.

[0056] Even though oxidized film may be formed on the surface of the platinum catalyst at the fuel and oxidizer electrodes without voltage application by the battery 5, application of the electrical potential by the battery 5 at Step S100 acts to decrease the catalytic activity further by making the oxidized film thicker. The oxidized film on the surface of the platinum catalyst becomes gradually exfoliated through regular operation of the fuel cell stack 1; however, the platinum regains its original condition from the inactive status when the electrical potential at the fuel electrode or oxidizer electrode becomes less than 0.8 V, and the platinum catalytic activity is recovered completely. That is, after the oxidized film is formed on the surface of the platinum catalyst at the

fuel electrode, the oxidized film at the fuel electrode may be subsequently exfoliated by supplying hydrogen to the fuel gas passage 37.

[0057] Figure 6 illustrates a graph showing the time-wise variation in fuel cell output voltage before and after application of an external voltage to the fuel cell electrode stack according to another embodiment of the present invention. Figure 6 shows the voltage change of the unit fuel cell 30 when hydrogen is supplied to the fuel electrode, air is supplied to the oxidizer electrode, and the unit fuel cell 30 is kept isolated from an electrical load (i.e. “unloaded” or “open” status) for 45 seconds. During this time, the open-end voltage shows 0.95 V. The open-end voltage indicates the catalyst activity. The higher the open-end voltage, the more active the catalyst activity. When the battery 5 applies more than 0 V electrical potential to the unit fuel cell 30, an oxidized film is formed on the surface of the platinum catalyst particles.

[0058] In this example, after 50 seconds, electrical potentials of 1.2 V, 1.1 V, 1.0 V were applied from an external power supply, and then the external power supply was removed, to measure the open-end voltage. As a result, the open-end voltage was the lowest when 1.2 V was applied, followed by 1.1 V and 1.0 V in order. That indicates that the higher the applied electrical potential, the lower the open-end voltage of the unit fuel cell 30 afterwards, which means the oxidized film was formed more extensively to decrease the catalyst activity. In the case of application of an electrical potential of 1.2 V, wherein the open-end voltage dropped the most, the open-end voltage reached a value as low as 0.89 V, which is 0.06 V lower than the original condition before the oxidized film was formed.

[0059] From the example, it is apparent that the higher the application voltage to the fuel cell stack 1 by the battery 5, the lower the catalyst activity. When the application voltage is too high, however, for example as high as 1.5–2.0 V (depending on the temperature of the fuel cell stack 1) per unit fuel cell 30, carbon in the catalyst layer 32 becomes oxidized and corroded due to the high applied electrical potential. Therefore the predetermined electrical potential, which means the application voltage by the Battery 5, is preferably set to about 1.2 V, which is the voltage of the fuel cell stack 1 consisting of stacked unit fuel cells 30.

[0060] Depending on the material and the molecular structure of the electrolyte film 31, when the electrolyte film 31 loses water and dries, the resistance of the electrolyte film 31 may be increased due to deterioration of the electrolyte film 31 by electrolysis of water. To prevent such situation, the predetermined voltage V1 must be lower than the water electrolysis voltage. It will be understood, however, that the predetermined electrical

potential V1 is not limited to 1.2 V, but rather, can be any potential that can form an oxidized film on the platinum catalyst without causing deterioration of the fuel cell stack 1 by water electrolysis.

[0061] Figure 7 illustrates a flowchart showing a sequence of steps used by the fuel cell control system of Fig. 3 when shutting-down the fuel cell system according to another embodiment of the present invention. When the fuel cell system is operating, the switch 22 is ON; the switch 23 is ON during charging from the fuel cell stack 1; it is turned OFF at other times. In addition, both of the compressor 2 and the recycle compressor 11 are in operation. When an operation stop signal for the fuel cell system is detected, Step S200 stops the compressor 2.

[0062] At Step S201, controller 40 turns off the recycle compressor 11, and stops the hydrogen supply from the compressed hydrogen storage container 3.

[0063] At Step S202, controller 40 applies a means and method to form an oxidized film on the active platinum catalyst prior to start-up of the fuel cell system. Step S202 turns ON the switch 23, applying the predetermined voltage V1 from the battery 5 to the fuel cell stack 1. When the compressed hydrogen supply is stopped according to Step S201, air from outside may diffuse into the fuel cell and mix with hydrogen at the fuel electrode. If air is mixed in at the fuel electrode, the hydrogen/air front B may form just as in fuel cell system start-up. In Step S202, an oxidized film is reversibly formed on the surface of the active platinum catalyst in the catalyst layer 32b at the oxidizer electrode (cathode) 32 by applying the predetermined voltage V1 to the fuel cell stack 1 from the battery 5.

[0064] At Step S203, controller 40 checks if the predetermined time T1 has elapsed since the switch 23 turned ON to apply an electrical potential from the battery 5. If the predetermined time T1 has elapsed, the electronic process controller 40 proceeds to Step S204.

[0065] At Step S204, controller 40 turns off the switch 23 to cease application of an electrical potential from the battery 5 to the fuel cell stack 1.

[0066] By the above-mentioned controls, when the fuel cell system is shutdown, carbon corrosion at the oxidizer electrode can be prevented by forming oxidized film on the surface of the active platinum catalyst in the catalyst layer 32b, even when air is mixed in at the fuel electrode. A reversibly oxidized film may also be formed on the surface of the active platinum catalyst in the catalyst layer 33b of the fuel electrode (anode) 33.

[0067] Figure 8 illustrates a graph showing fuel cell voltage characteristics as a function of current density for an exemplary unit fuel cell 30 in the fuel cell stack 1. The logarithm of the current density and the voltage are proportional, with slope of about 90 mV/decade of current density. That is, when the current density changes from i_1 to i_2 , the voltage decrease ΔE is expressed as below:

$$\Delta E = 0.09 \times \log(i_2/i_1). \quad (\text{Equation 6}).$$

[0068] When the application voltage is 1.2 V and the open-end voltage drop is 0.06 V, the effective catalyst surface area which shows catalytic activity before application of an external electrical potential is expressed as A_1 (cm²), and the effective surface area which shows catalytic activity after forming the oxidized film on the catalyst surface is expressed as A_2 (cm²). Even in this case, minimal current exists; the current before application of the external electrical potential is expressed as I_1 (A), while the current after application of the external electrical potential is expressed as I_2 (A). Here i_1 and i_2 are related to I_1 and I_2 as follows:

$$i_1 = I_1/A_1 \quad (\text{Equation 7}).$$

$$i_2 = I_2/A_2. (\text{Equation 8})$$

Now, at steady state, there is no change in current before and after application of the external electrical potential. Therefore:

$$I_1 = I_2. \quad (\text{Equation 9}).$$

$$A_2/A_1 = i_1/i_2. \quad (\text{Equation 10}).$$

[0069] According to Equation 6:

$$A_2/A_1 = i_1/i_2 = 1/10^{(0.06/0.09)} = 0.22 \quad (\text{Equation 11}).$$

This means that when an externally applied electrically potential of 1.2 V is applied to the fuel cell stack 1, the voltage is decreased by 0.06 V, corresponding to a loss of 78% of the effective surface area which shows catalyst activity. That means that almost 80% of the catalyst becomes inactive. Therefore, one can prevent carbon corrosion and deterioration at the oxidizer electrode, even when supplying hydrogen to the fuel electrode when air is present at the fuel electrode. The calculation above is only one example of an

embodiment for carrying out of this invention; it does not limit the scope of the invention to the calculated values used in the above example.

[0070] In one embodiment, illustrated by Figure 8, an oxidized film is formed on the surface of the catalyst layer 32 at the oxidizer electrode, thereby reversibly decreasing the activity of the platinum catalyst or making the catalyst inactive, by applying an electrical potential to the fuel cell stack 1 with the battery 5 during fuel cell system start-up. Even if air is mixed in at the fuel electrode when stopped, and the hydrogen/air front B is produced at the fuel electrode by supplying hydrogen to the fuel electrode at start-up, one can prevent oxidation and corrosive reactions of the carbon catalyst support at the oxidizer electrode because of the presence of the oxidized film on the platinum catalyst surface of the catalyst layer 32 at the oxidizer electrode.

[0071] Also, when the fuel cell system is shutdown, one can prevent the oxidation and corrosion reaction of the carbon catalyst support by creating an oxidized film on the platinum catalyst surface of the catalyst layer 32 at the oxidizer electrode with an applied electrical potential from the battery 5. By applying the electrical potential to the fuel cell stack 1 with the battery 5, the oxidized film can be formed more rapidly on the platinum catalyst surface of the catalyst layer 32 at the oxidizer electrode. This can prevent the oxidation and corrosion reaction at the carbon catalyst support of the oxidizer electrode, and thereby decrease the start-up time of the fuel cell.

[0072] In addition, because the applied electrical potential from the battery 5 is lower than the water electrolysis electrical potential, the system may prevent drying out of the electrolyte film 31, prevent the resistance increase of the electrolyte film 31, and prevent the deterioration of the electrolyte film 31. The fuel cell system may also be reduced in size by using as an external source of electrical potential a battery 5 that stores excess power generated by the fuel cell stack 1.

[0073] Figure 9 illustrates a schematic drawing of a fuel cell control system operating in fuel cell shutdown mode according to another embodiment of the present invention. In this embodiment, a three-way valve 26 is shown downstream of the compressor 2. With this configuration, the compressor 2 can be connected to the compressed hydrogen supply passage 9 to supply air to the fuel cell. In addition, the three-way valve 26 connects the compressor 2 to the oxidizer electrode of the fuel cell stack 1 in regular operation of the fuel cell system. Since other operation controls of the fuel cell system of Figure 9 at start-up are the same as in Figure 3, there description is omitted here.

[0074] Figure 10 illustrates a flowchart showing a sequence of steps used by the fuel cell control system of Fig. 9 when shutting-down the fuel cell system according to another embodiment of the present invention. Operation controls from Step S300 to Step S303 are the same as in Step S200 to S203 in Figure 4, and are omitted here.

[0075] Step S304 turns off the switch 23 to cease application of the electrical potential from the battery 5 to the fuel cell stack 1.

[0076] Step S305 switches the three-way valve 26 to permit passage of compressed hydrogen from the compressor 2 to the compressed hydrogen supply passage 9. This enables air to be supplied to the fuel electrode of the fuel cell stack 1 from the compressor 2 via the hydrogen supply passage 9. In addition to three-way valve 13, the fuel electrode can be connected to the external air environment by passing air through the fuel cell stack 1 and the hydrogen supply passage 9.

[0077] Step S306 purges substantially all of the remaining hydrogen in the fuel cell electrode assembly by starting the compressor 2. The purged hydrogen is consumed by the optional hydrogen consuming device 15. Even though the oxidized film is formed on the platinum catalyst surface of the catalyst layer 32b of the oxidizer electrode by Step S303, the hydrogen/air front B exists for a long time at the fuel electrode if hydrogen is left there for an extended period of time. In this case, the oxidized film on the platinum catalyst surface is exfoliated as time elapses. But after forming the oxidized film on platinum catalyst surface of the oxidizer electrode by purging hydrogen at the fuel electrode with compressor 2, deterioration of the fuel cell stack 1 during long shutdown intervals of the fuel cell system can be prevented.

[0078] Step S307 checks if the predetermined time T2 has elapsed since the compressor 2 began to purge the fuel electrode. If the predetermined time T2 has elapsed, the electronic process controller proceeds to Step S308. The predetermined time T2 corresponds to the time required to purge hydrogen from the fuel electrode, which is set at 10 seconds for the present example. It should be noted, however, that the predetermined time T2 is not limited to 10 seconds, but rather, corresponds to the time required to purge hydrogen from the fuel electrode. The predetermined time T2 will depend on the number, volume and electrode assembly area of the unit fuel cells making up the fuel cell system.

[0079] Step S308 stops the compressor 2 and switches the three-way valve 26 to permit passage of gas from the compressor 2 to the oxidizer electrode, or closes the three-way valve 26 completely to cease fuel cell power generation and shut down the fuel cell system. By use of the above fuel cell systems and control methods to form an oxidized

film on the platinum catalyst and purge hydrogen from the fuel cell electrode assembly, one can prevent or reduce deterioration of the fuel cell stack 1 during periods of extended fuel cell system shutdown.

[0080] In the embodiment illustrated by Figure 9, an oxidized film is formed on the surface of the catalyst layer 32 at the oxidizer electrode, thereby reversibly decreasing the activity of the platinum catalyst or making the catalyst inactive, by applying an electrical potential to the fuel cell stack 1 with the battery 5 during fuel cell system shutdown. In addition to the beneficial effects of the previously described preferred embodiment of Fig. 8, the presently more preferred embodiment can prevent additional deterioration of the carbon catalyst support by oxidation and corrosion reactions at the oxidizer electrode during periods of extended fuel cell system shutdown, by forming an oxidized film on the platinum catalyst surface and then supplying air from the compressor 2 to the fuel electrode assembly to purge substantially all of the remaining hydrogen from the fuel electrode, thereby preventing deterioration of the fuel cell stack 1.

[0081] A third embodiment of the presently disclosed invention is illustrated in Figure 11. Since the composition and construction of the fuel cell system in this embodiment is the same as in the first embodiment, the detailed descriptions are omitted here. Operation controls of this embodiment are described by the flowchart in Figure 11. The flowchart of Figure 11 shows the control actions corresponding to decreasing the required output power for the fuel cell stack 1.

[0082] At Step S400, the voltage V of the fuel cell stack 1, that is, the required power demand for the fuel cell stack 1, is detected by the voltage sensor 17.

[0083] At Step S401, the voltage V detected at Step S400 is compared with a predetermined voltage (the second predetermined voltage) V2. Although the details are described later in this disclosure, the predetermined voltage V2 is that at which the active platinum of catalyst layer 32b dissolves by the reaction shown in Equation (12) below (assumed to be 0.88 V here):



[0084] When the voltage V is higher than the predetermined voltage V2, move on to Step S402. On the other hand, when the voltage V is lower than the predetermined voltage V2, generate power in order to achieve the required power for the fuel cell stack 1.

[0085] As the fuel cell system enters, for example, an idling condition, and the voltage V of the fuel cell stack 1 exceeds the predetermined voltage V2, the dissolution of platinum as shown in Equation (12) can occur. Therefore, at Step S402, switch 23 is turned ON, and the battery 5 applies voltage stepwise so that the fuel cell stack 1 becomes the predetermined voltage V1 to form an oxidized film instantly on the platinum surface of the catalyst layer 32b of the oxidizer electrode 32. The predetermined voltage V1 is that required for forming an oxidized film on the platinum surface of the catalyst layer 32b, and is assumed to be 1.2 V in the Example. Forming an oxidized film on the platinum surface of the catalyst layer 32b inhibits dissolution of active catalyst platinum metal of the catalyst layer 32b, even when the oxidizer electrode is at high potential.

[0086] When applying voltage to the fuel cell stack 1 while gradually increasing the voltage, the dissolution of platinum as shown in Equation (12), occurs in the catalyst layer 32b during this period until an oxidized film is formed on the platinum surface.

However, when applying the predetermined voltage V1 to the fuel cell stack 1 using the battery 5, it is possible to instantly form an oxidized film on the surface of the catalyst layer 32b and inhibit dissolution of platinum, by applying the predetermined voltage V1 stepwise. This is because once forming an oxidized film on the platinum surface, the dissolution of platinum as shown in Equation (12) (below) does not occur.

[0087] At Step S403, the time for applying the predetermined voltage V1 to the fuel cell stack 1 is calculated. When the calculated time T passes a predetermined time T3, move on to Step S404. The predetermined time T3 is the amount of time for an oxidized film to be formed on the surface of the catalyst layer 32b platinum, and is assumed to be 0.5 seconds here.

[0088] At Step S404, Switch 23 is turned OFF to terminate the voltage application to the fuel cell stack 1 by the battery 5.

[0089] Step S405 determines if an operation stop signal of the fuel cell system is received. When stopping the fuel cell system, move on to Step S406. If not, continue to generate power according to the required power for the fuel cell stack 1.

[0090] At Step S406, stop the recycle compressor 11 to terminate the hydrogen supply from the hydrogen cylinder 3 and air supply from the compressor 2. As an oxidized film is formed on the platinum surface of the catalyst layer 32b when stopping the fuel cell system, it is possible to inhibit dissolution of platinum in the catalyst layer 32b which is at high potential at the time of stopping the fuel cell system, and further inhibit carbon corrosion which may possibly occur when stopping the fuel cell system.

[0091] When the required power for the fuel cell stack 1 is decreased by the above-mentioned controls, that is, when the voltage at the fuel cell stack 1 is increased, it enables the formation of an oxidized film on the platinum surface of the catalyst layer 32b which is at high potential and inhibits platinum dissolution, by applying voltage to the fuel cell stack 1 with the battery 5.

[0092] Next, the setting method of the predetermined voltage V2 will be described.

Figure 12 is a map showing changes in voltage over time, when changing the voltage of the unit cell 30 from 0.5 V to 1.0 V stepwise. Such changes in voltage were conducted in the case of 0.5 V to 0.85 V, 0.5 V to 0.88 V, 0.5 V to 0.91 V, 0.5 V to 0.95 V, 0.5 V to 1.0 V, and 0.5 V to 1.2 V. Briefly, the unit cell 30 was varied from high power to low power in six patterns. This cycle was repeated 3,000 times. Figure 13 indicates the relation of the changed voltage and the decreased amount of generated voltage of the unit cell 30 per 1,000 cycles.

[0093] According to this, when the voltage of the unit cell 30 increases, that is, when the unit cell 30 is changed from high power to low power, the decreased amount of generated voltage increases as the voltage increases to over 0.88 V. When the voltage is approximately 0.92 V, the decreased amount of generated voltage of the unit cell 30, that is, the deterioration, is maximized. In addition, when increasing the voltage of the unit cell 30 to more than 0.92 V, deterioration decreases. This is because when changing the voltage of the unit cell 30 stepwise, an oxidized film is instantly formed on the platinum surface of the catalyst layer 32b of the unit cell 30, and especially when the voltage exceeds 0.92 V, dissolution of platinum as shown in Equation (12) is inhibited.

[0094] From the said results, since it is desirable to set the predetermined voltage V1 to be over 0.93 V, the predetermined voltage is assumed to be 1.2 V in this embodiment. Meanwhile, the predetermined voltage V2 is assumed to be 0.88 V. Operation controls of this embodiment may be used in the fuel cell system of embodiment 2.

[0095] In this embodiment, when the required power for the fuel cell stack 1 is decreased, for example, at the time of idling, that is, when the voltage of the fuel cell stack 1 is increased, an oxidized film is formed on the platinum surface of the catalyst layer 32b that is at high potential, by applying voltage to the fuel cell stack 1 with the battery 5. By forming an oxidized film on the platinum of the catalyst layer 32b, it enables inhibition of the dissolution of platinum and deterioration of the fuel cell stack 1, even when the catalyst layer 32b is at high potential.

[0096] By applying voltage stepwise with the battery 5, it enables the instant formation of an oxidized film on the platinum surface of the catalyst layer 32b. It is also possible to inhibit dissolution of platinum of the catalyst layer 32b, even when the catalyst layer 32b is at high potential.

[0097] In addition, when stopping the fuel cell system later, it allows inhibition of carbon corrosion generated while the fuel cell system stops, by forming an oxidized film on the platinum surface of the catalyst layer 32b.

[0098] Next, embodiment 4 of the present invention will be described. Since the composition of the fuel cell system in this embodiment is the same as in embodiment 1, detailed descriptions are omitted. Operation controls in this embodiment are described according to a flowchart in Figure 14. The flowchart of Figure 14 indicates control actions when the required power for the fuel cell stack 1 is decreased.

[0099] At Step S500, the voltage V of the fuel cell stack 1, that is, the required power for the fuel cell stack 1, is detected by the voltage sensor 17.

[00100] At Step S501, the voltage V detected from Step S500 is compared with a predetermined voltage V2. In addition, when the voltage V is higher than the predetermined voltage V2, move on to Step S502. On the other hand, when the voltage V is lower than the predetermined voltage V2, that is, the required power for the fuel cell stack 1 is relatively high, power is generated in order to achieve the required power for the fuel cell stack 1.

[00101] At Step S502, the voltage V detected from Step S500 is compared with a predetermined voltage (the third voltage) V3. When the voltage V is lower than the predetermined voltage V3, move on to Step S506. On the other hand, when the voltage V is higher than the predetermined voltage V3, move on to Step S503. As shown in Figure 13, when the voltage of the unit cell 30 is between 0.88 V and 0.92 V, the decreased amount of power voltage increases rapidly. That is, when the unit cell 30 is at high potential between 0.88 V and 0.92 V, it facilitates dissolution of platinum in the catalyst layer 32b and deterioration of the unit cell 30 significantly progresses. Therefore, in this embodiment, the predetermined voltage is assumed to be 0.90 V. If the voltage V is higher than the predetermined voltage V3, it is assumed that considerable dissolution of platinum is occurring.

[00102] At Step S503, electric power is taken out of the fuel cell stack 1 by Load (4) to set the voltage of the fuel cell stack 1 to a predetermined voltage V4 which is lower

than the predetermined voltage V3. The electric power taken from the fuel cell stack 1 may be charged in the battery 5.

[00103] Figure 15 shows a cyclic voltammogram in which the potential of the oxidizer electrode against the relative hydrogen electrode was swept from 0.04 V to 0.9 V under the condition of supplying hydrogen to the fuel electrode and nitrogen to the oxidizer electrode of the unit cell 30. According to this voltammogram, when decreasing the electric potential from 0.9 V, the reduction reaction of platinum ions shown in Equation (13) occurs and the reduction current runs:



For the reaction of Equation (13), the reduction current density increases around 0.8 V. Briefly, at Step S503, by setting the voltage of the fuel cell stack 1 to be 0.8 V, the reduction reaction of platinum ions occurs as shown in Equation (13), thereby reducing generation of platinum ions by dissolution of platinum according to the undesirable reaction shown in Equation (12)

This may inhibit deterioration of the fuel cell stack 1. Therefore, the predetermined voltage V4 is assumed to be 0.8 V. This enables a reduction in the amount of platinum ions that are dissolved due to the high potential of the catalyst layer 32b in order to generate platinum.

[00104] At Step S504, when the time T that the voltage of the fuel cell stack 1 is assumed as the predetermined voltage V4 passes a time T4, move on to Step S505. The predetermined time T4 is the period of time for reducing platinum ions to generate platinum. By extending the time, it enables the reduction of platinum ions into platinum. However, if the predetermined time T4 is extended, the efficiency of the fuel cell system decreases. Accordingly, in this embodiment, the time is predetermined to be 1 second.

[00105] Step S505 stops taking the electric power out of the fuel cell stack 1 by Load (4) (Steps S503 to S505 constitute a catalyst reduction means).

[00106] Since Steps S506 to S510 are the same controls as Steps S402 to S406 in embodiment 3, the descriptions are omitted here.

[00107] When the said controls become lower than the required power for the fuel cell stack 1 and the voltage becomes higher than the predetermined voltage V3, reduce the voltage of the unit cell 10 once. This enables inhibition of the deterioration of the catalyst layer 32b and the fuel cell stack 1 by reducing platinum ions generated from

dissolution of platinum due to the high potential of the catalyst layer 32b and then returning the platinum ions into platinum.

[00108] When the power of the fuel cell stack 1 is found to be low for a long period after monitoring by the voltage sensor 17, that is, when the high voltage condition of the fuel cell stack 1 is maintained, controls from Steps S503 to S505 may be conducted and platinum ions may be reduced in the catalyst layer 32b to return the platinum ions into platinum. This allows inhibition of the degradation of the catalyst layer 32b.

[00109] The effects of embodiment 4 of the present invention will be described. In this embodiment, when the required power for the fuel cell stack 1 decreases, that is, when the voltage of the fuel cell stack 1 becomes higher than the predetermined voltage V3, the voltage of the fuel cell stack 1 is reduced to the predetermined voltage V4 by e.g. the load (4). This enables the reduction of platinum ions generated due to the high potential of the catalyst layer 32b and returns the platinum ions into platinum. As a result, deterioration of the catalyst layer 32b is inhibited. In addition, since an oxidized film is formed after returning the platinum ions to platinum, the oxidized film can inhibit the dissolution of platinum, thereby improving the fuel cell life.

[00110] It should be understood by one skilled in the art that by specifying an order in the present disclosure (e.g., order of steps to be performed, order of layers on a surface, specific materials included in a composition or layer, and the like), it is not intended to preclude intermediate steps or layers, additional steps, layers or materials, or variations in the number or types of steps, layers or materials, as long as the disclosed steps or material layers appear in the order as specified. All possible modifications or improvements of the invention within the scope of this written technological disclosure are intended to be included within the scope of the claimed invention. In particular, this invention is not limited to the disclosed examples or preferred embodiments described within the written disclosure. Various embodiments of the invention have been described. These and other embodiments are within the scope of the following claims.

CLAIMS:

1. A fuel cell system comprising:
a fuel cell including a fuel electrode, an oxidizer electrode, an electrolyte film between the fuel electrode and the oxidizer electrode, and a first catalyst layer comprising a first catalyst having a first oxidized surface situated between the electrolyte film and the oxidizer electrode, wherein the first oxidized surface is formed by reversible oxidation at the time of starting-up or shutting-down the fuel cell.
2. The fuel cell system of claim 1, further comprising a second catalyst layer comprising a second catalyst having a second oxidized surface situated between the electrolyte film and the fuel electrode, wherein the second oxidized surface is formed by reversible oxidation at the time of starting up or shutting down the fuel cell.
3. The fuel cell system of claim 1, wherein the first catalyst layer comprises a redox catalyst supported on a catalyst support.
4. The fuel cell system of claim 3, wherein the redox catalyst comprises one or more metal selected from the group consisting of platinum, palladium and rhenium.
5. The fuel cell system of claim 3, wherein the catalyst support comprises carbon.
6. The fuel cell system of claim 1, wherein the first oxidized catalyst surface exhibits decreased catalytic activity relative to the first catalyst surface in a non-oxidized state.
7. The fuel cell system of claim 1, wherein oxidation of the first catalyst surface includes application of a first voltage to the fuel electrode and oxidizer electrode, and wherein the oxidizer electrode is used as an anode, before supplying hydrogen to the fuel electrode at the time of starting-up the fuel cell.
8. The fuel cell system of claim 7, wherein the first voltage is less than a voltage required to cause water electrolysis within the fuel cell.

9. The fuel cell system of claim 7, wherein the first voltage is greater than an oxidation voltage of the first catalyst.
10. The fuel cell system of claim 7, wherein the first voltage is applied in a stepwise manner.
11. The fuel cell system of claim 7, further comprising a voltage detection means for measuring a voltage across the fuel electrode and oxidation electrode of the fuel cell, and wherein the first oxidized surface is formed on the first catalyst when the measured voltage exceeds a second voltage.
12. The fuel cell system of claim 11, further comprising a catalyst reducing means for reducing the oxidation state of the first catalyst when the voltage across the fuel electrode and oxidation electrode electrodes exceeds a third voltage that is greater than the second voltage.
13. The fuel cell system of claim 12, wherein the first voltage is applied to the fuel electrode and oxidizer electrode after reducing the oxidation state of the catalyst using the catalyst reducing means.
14. The fuel cell system of claim 12, wherein the third voltage is greater than a voltage at which the first catalyst is ionized.
15. The fuel cell system of claim 11, wherein the second voltage is greater than 0.88 volts.
16. The fuel cell system of claim 7, wherein the first voltage is applied using a secondary cell adapted to store a portion of the electrical power generated by the fuel cell.
17. The fuel cell system of claim 16, wherein the secondary cell is a battery.

18. The fuel cell system of claim 1, wherein oxidation of the first catalyst surface includes application of a voltage to the fuel electrode and oxidizer electrode, and wherein the oxidizer electrode is used as an anode, at the time of shutting-down the fuel cell.
19. The fuel cell system of claim 18, wherein the fuel electrode is purged with air at the time of shutting-down the fuel cell.
20. The fuel cell system of claim 18, wherein the first voltage is less than a voltage required to cause water electrolysis within the fuel cell.
21. The fuel cell system of claim 18, wherein the first voltage is greater than an oxidation voltage of the first catalyst.
22. The fuel cell system of claim 18, wherein the first voltage is applied in a stepwise manner.
23. The fuel cell system of claim 18, further comprising a voltage detection means for measuring a voltage across the fuel electrode and oxidation electrode of the fuel cell, and wherein the first oxidized surface is formed on the first catalyst when the measured voltage exceeds a second voltage.
24. The fuel cell system of claim 23, further comprising a catalyst reducing means for reducing the oxidation state of the first catalyst when the voltage across the fuel electrode and oxidation electrode electrodes exceeds a third voltage that is greater than the second voltage.
25. The fuel cell system of claim 24, wherein the first voltage is applied to the fuel electrode and oxidizer electrode after reducing the oxidation state of the catalyst using the catalyst reducing means.
26. The fuel cell system of claim 24, wherein the third voltage is greater than a voltage at which the first catalyst is ionized.

27. The fuel cell system of claim 23, wherein the second voltage is greater than 0.88 volts.
28. The fuel cell system of claim 18, wherein the first voltage is applied using a secondary cell adapted to store a portion of the electrical power generated by the fuel cell.
29. The fuel cell system of claim 28, wherein the secondary cell is a battery.
30. A method of operating a fuel cell, including the steps of:
providing a source of fuel to a power generating fuel cell including a fuel electrode, an oxidizer electrode, an electrolyte film between the fuel electrode and the oxidizer electrode, a first catalyst layer comprising a first catalyst surface situated between the electrolyte film and the oxidizer electrode;
stopping the source of fuel to the fuel cell; and
reversibly forming a first oxidized layer on the first catalyst surface.
31. The method of claim 30, wherein the fuel cell further comprises a second catalyst layer between the electrolyte film and the fuel electrode, wherein the second catalyst layer comprises a second catalyst surface having a second oxidized layer, and wherein the second oxidized layer is formed at the time of starting up or shutting down the fuel cell.
32. The method of claim 30, wherein the fuel electrode is purged with air after stopping the source of fuel to the fuel cell.
33. The method of claim 30, further including the step of resuming power generating operation of the fuel cell subsequent to reversibly forming the first oxidized layer on the first catalyst surface.
34. The method of claim 30, wherein each of the steps is carried out under the direction of an electronic process controller.
35. The method of claim 30, wherein the first oxidized layer on the first catalyst surface is reversibly formed by application of a first voltage to the fuel electrode and oxidizer electrode, and wherein the oxidizer electrode is used as an anode, at the time of shutting-down the fuel cell.

36. The method of claim 35, wherein the first voltage is less than a voltage required to cause water electrolysis within the fuel cell.
37. The method of claim 35, wherein the first voltage is greater than an oxidation voltage of the first catalyst.
38. The method of claim 35, wherein the first voltage is applied in a stepwise manner.
39. The method of claim 35, wherein a voltage across the fuel electrode and oxidation electrode of the fuel cell is measured, and wherein the first oxidized surface is formed on the first catalyst when the measured voltage exceeds a second voltage.
40. The method of claim 39, wherein a reducing means is used to reduce the oxidation state of the first catalyst when the voltage across the fuel electrode and oxidation electrode exceeds a third voltage that is greater than the second voltage.
41. The method of claim 40, wherein the first voltage is applied to the fuel electrode and oxidizer electrode after reducing the oxidation state of the catalyst using the catalyst reducing means.
42. The method of claim 40, wherein the third voltage is greater than a voltage at which the first catalyst is ionized.
43. The method of claim 39, wherein the second voltage is greater than 0.88 volts.
44. The method of claim 35, wherein the first voltage is applied using a secondary cell adapted to store a portion of the electrical power generated by the fuel cell.
45. The method of claim 44, wherein the secondary cell is a battery.

46. A fuel cell system with a fuel cell that has an electrolyte film and includes a fuel electrode and an oxidizer electrode that have a catalyst layer holding a catalyst between the said electrolyte film and the electrodes, the said fuel cell system comprising an oxidized film producing means for forming an oxidized film on the said catalyst at the time of starting-up or shutting-down of the said fuel cell.

47. A fuel cell system according to claim 46, wherein the said oxidized film producing means is a voltage application means for applying a first voltage to the said fuel cell using the said oxidizer electrode as anode and forming an oxidized film on the said catalyst.

48. A fuel cell system according to claim 47, wherein the said oxidized film producing means applies the said first voltage using the said oxidizer electrode as anode and forms an oxidized film on the said catalyst, at the time of starting-up of the said fuel cell, prior to supplying hydrogen to the said fuel electrode.

49. A fuel cell system according to claim 47 or 48, wherein the said fuel cell system comprises an air supply means for supplying air to the said fuel electrode, and purges the said fuel electrode by the said air supply means using the said air at the time of shutting-down of the said fuel cell, after applying the said first voltage to the said fuel cell.

50. A fuel cell system according to claim 47 or 48, wherein the said first voltage is lower than the water electrolysis voltage.

51. A fuel cell system according to claim 47 or 48, wherein the said first voltage is higher than the oxidization voltage of the said catalyst.

52. A fuel cell system according to claim 47 or 48, wherein the said fuel cell system comprises a voltage detection means to detect the voltage of the said fuel cell, and the said oxidized film producing means forms an oxidized film on the said catalyst, when the voltage detected by the said voltage detection means is higher than a second voltage.

53. A fuel cell system according to claim 52, wherein the said fuel cell system comprises a catalyst reducing means for reducing the ionized form of said catalyst into the catalyst by lowering the voltage of the said fuel cell to the voltage for reducing the ionized form of said catalyst into the said catalyst, when the said voltage detected by the said voltage detection means is higher than a third voltage that is higher than the said second voltage.

54. A fuel cell system according to claim 53, wherein the said oxidized film producing means applies voltage to the said fuel cell after reducing the said ionized catalyst into the said catalyst by the said catalyst reducing means.

55. A fuel cell system according to claim 54, wherein the said third voltage is higher than the voltage at which the said catalyst is ionized.

56. A fuel cell system according to claim 52, wherein the said second voltage is over 0.88 volts.

57. A fuel cell system according to claim 52, wherein the said voltage application means applies voltage stepwise.

58. A fuel cell system according to claim 52, wherein the said voltage application means is a secondary cell which stores part of the electric power generated by the said fuel cell.

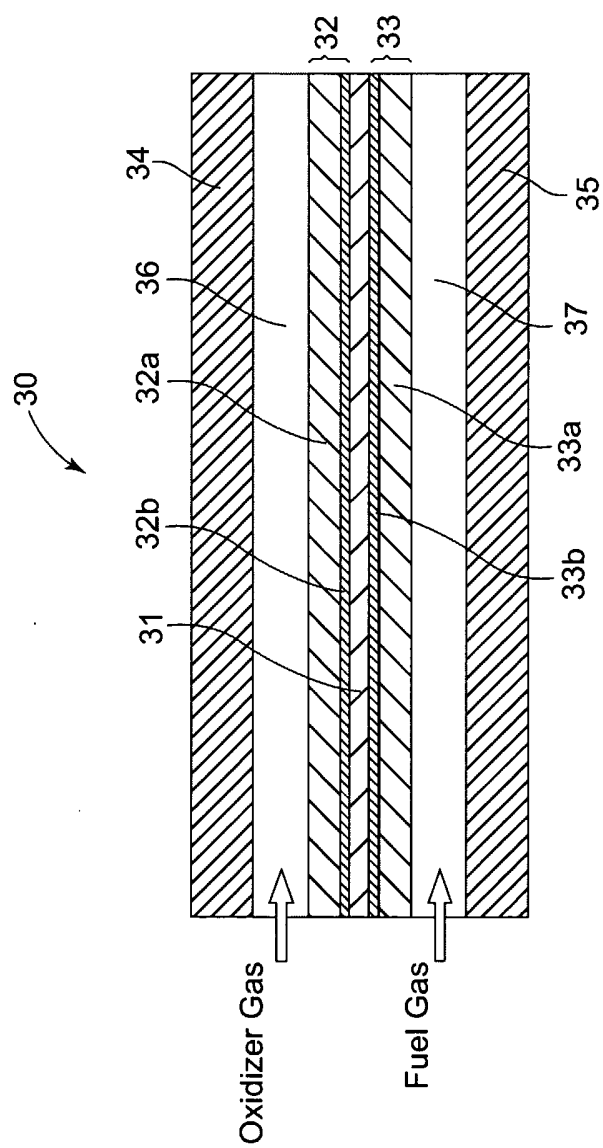


FIG. 1

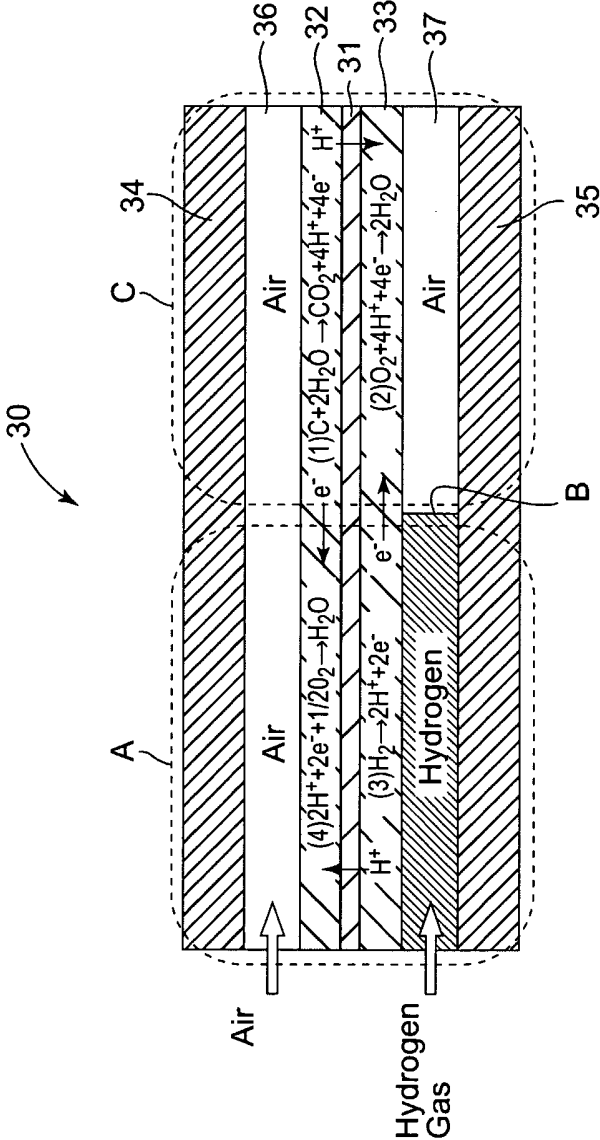


FIG. 2

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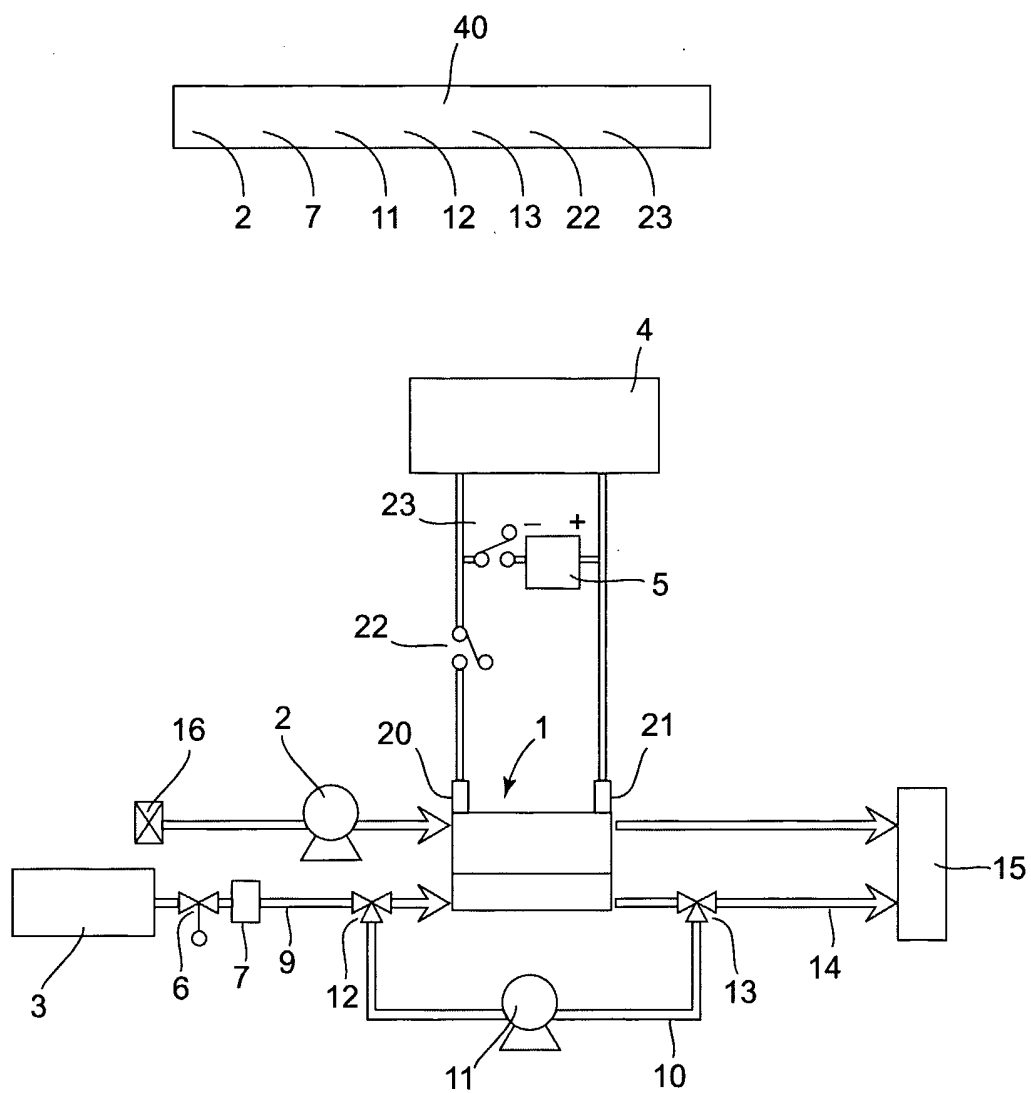


FIG. 3

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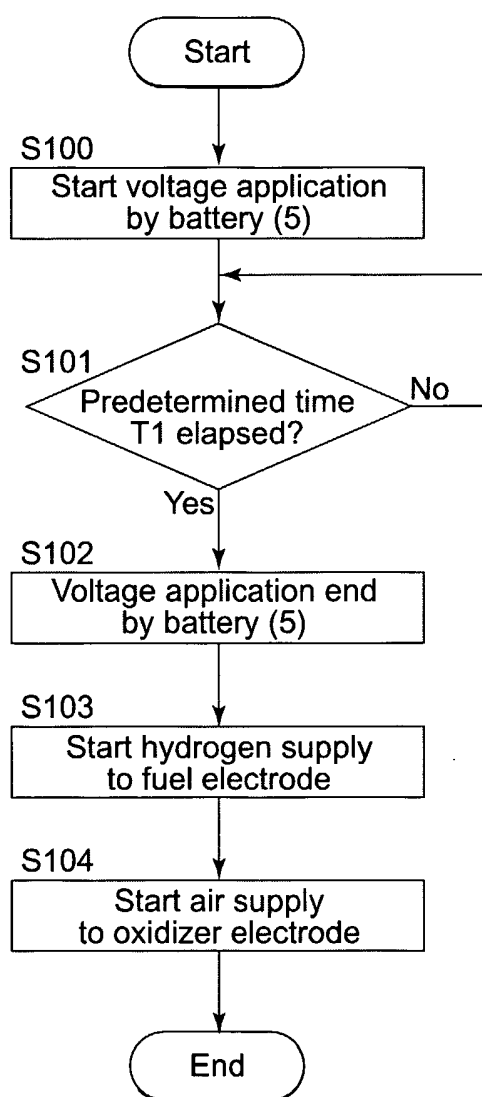


FIG. 4

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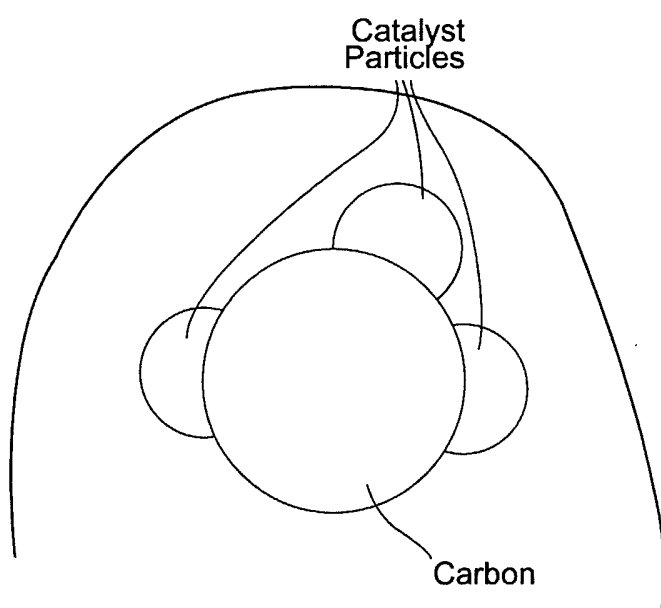


FIG. 5A

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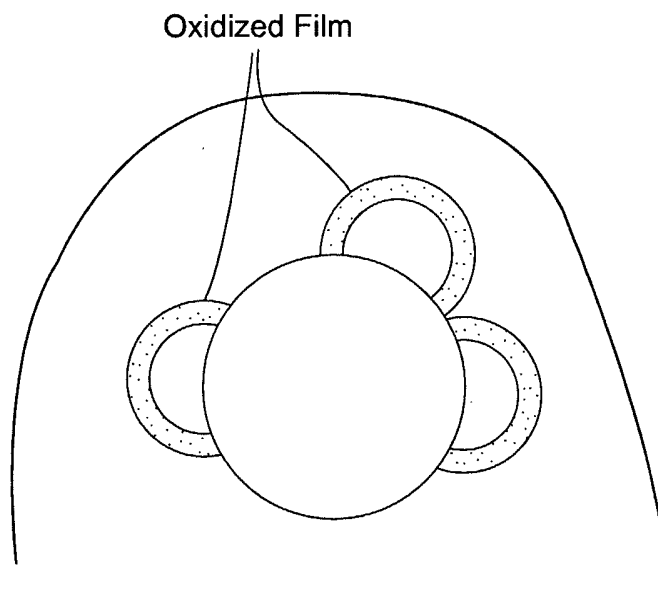


FIG. 5B

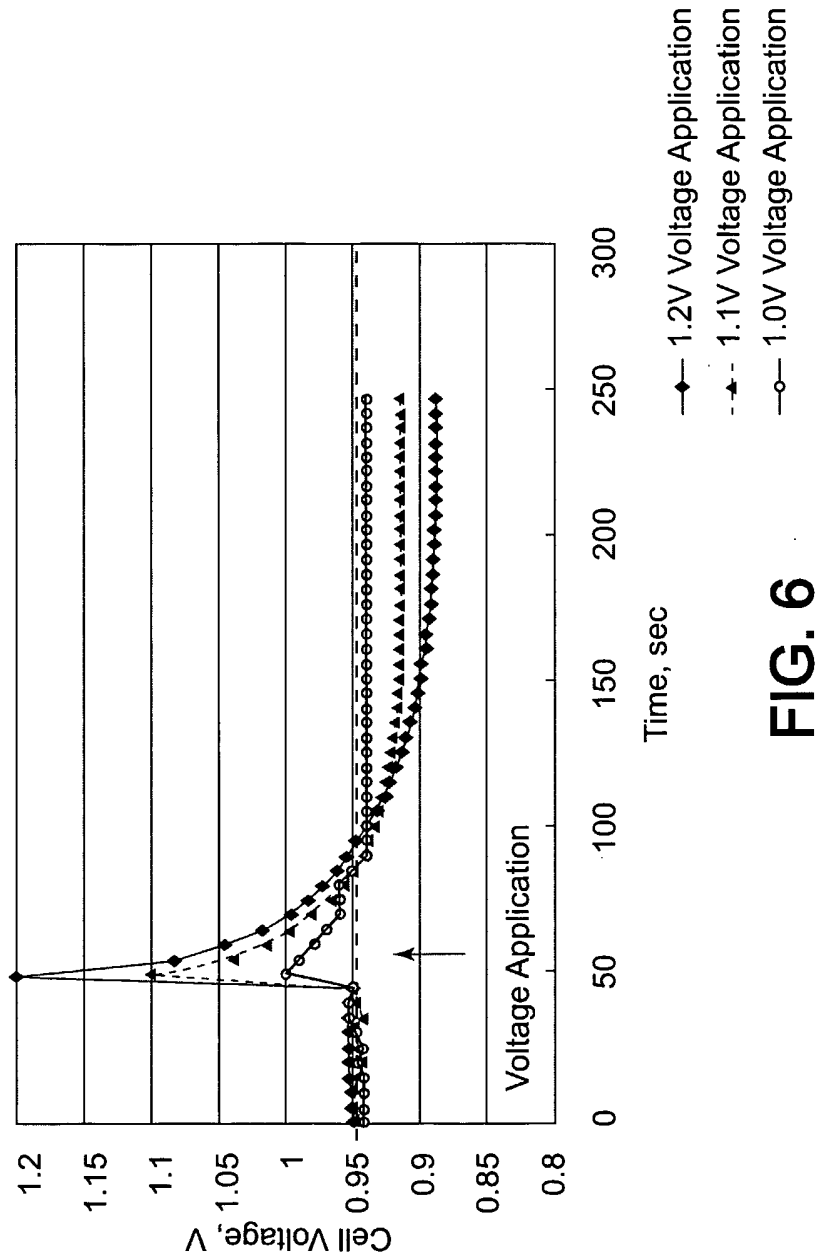


FIG. 6

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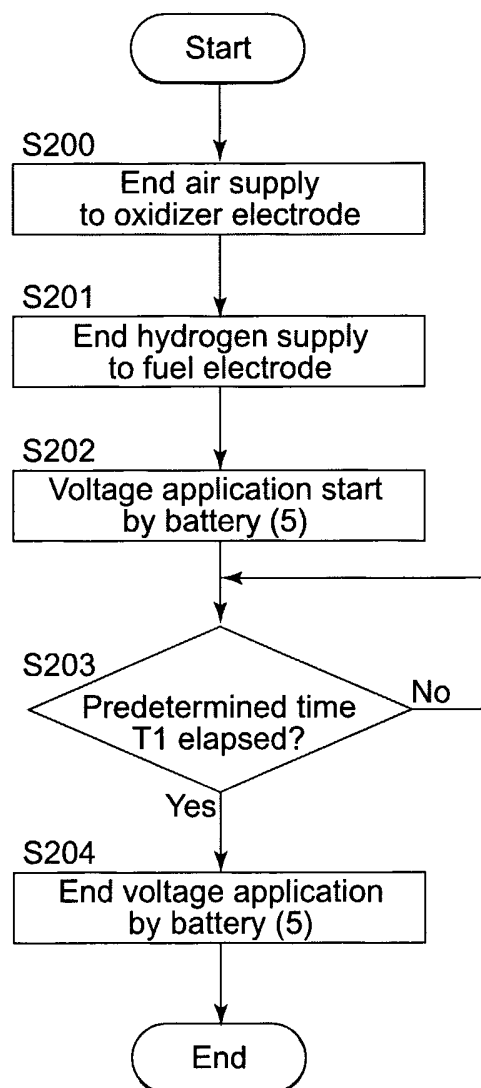


FIG. 7

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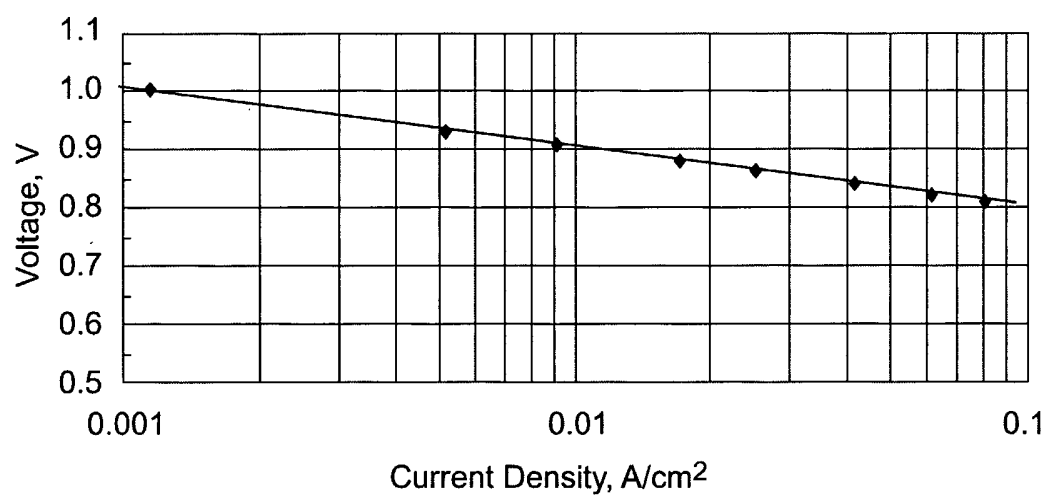


FIG. 8

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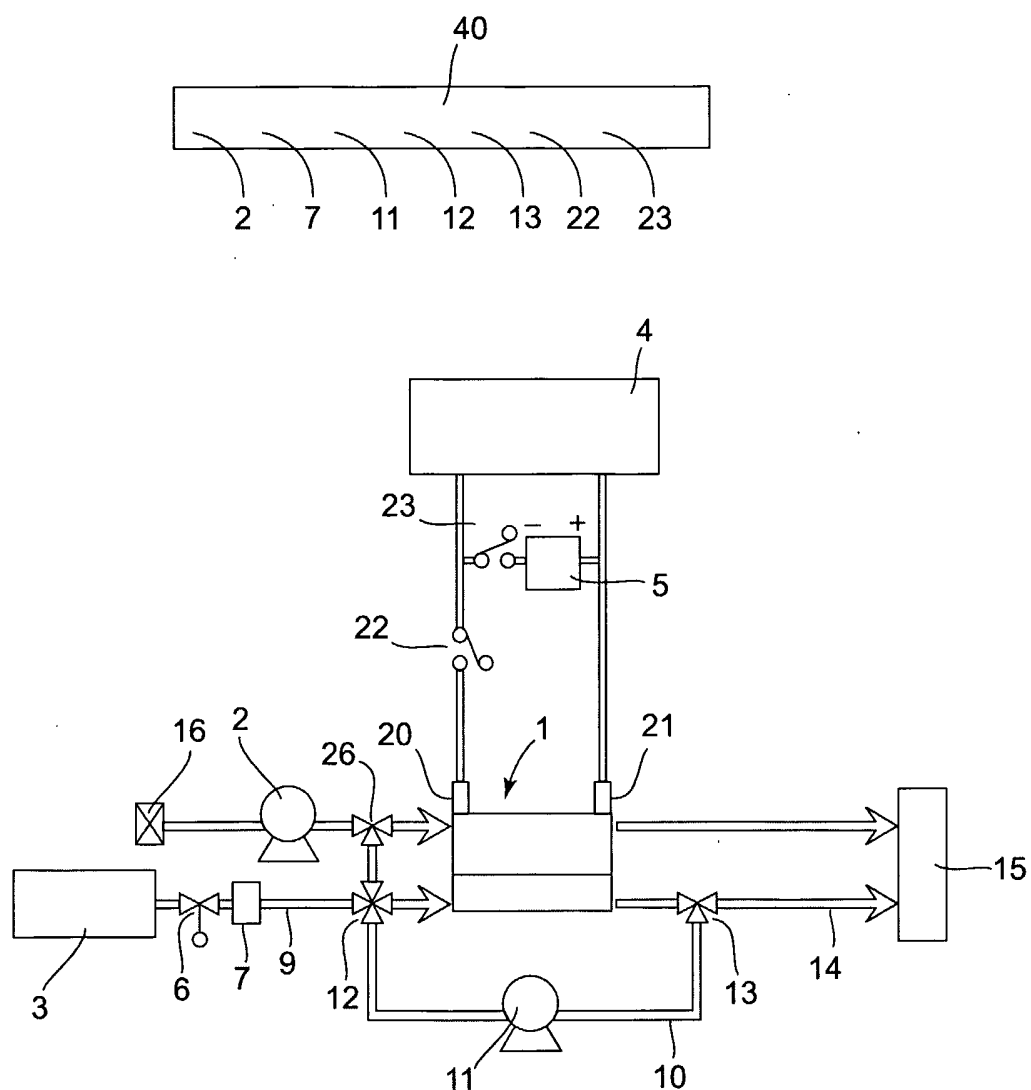


FIG. 9

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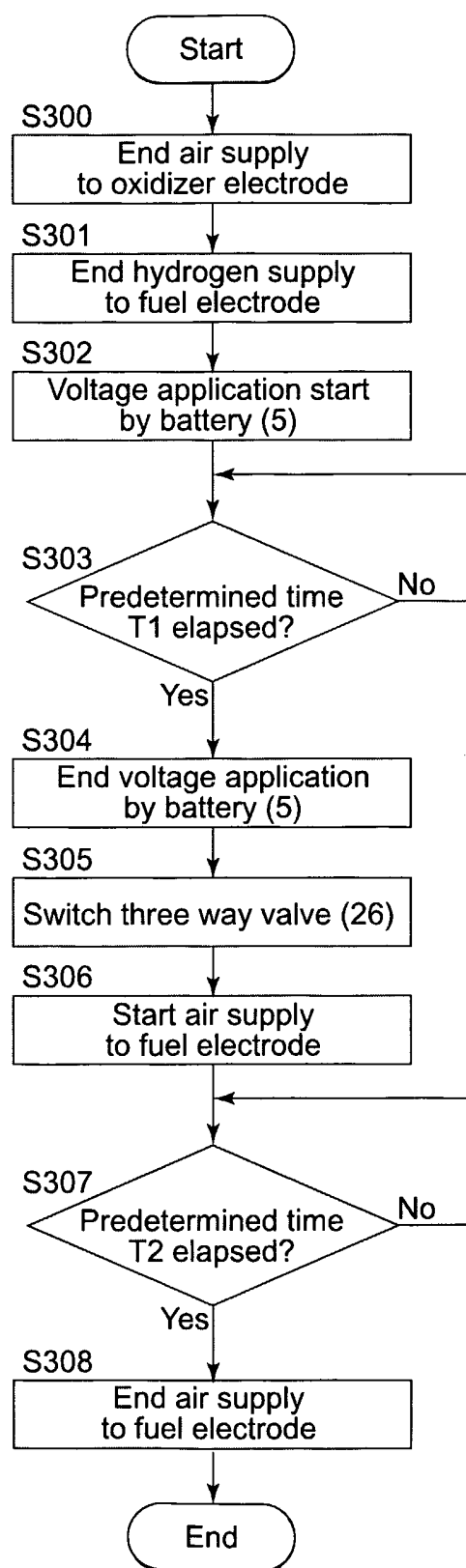


FIG. 10

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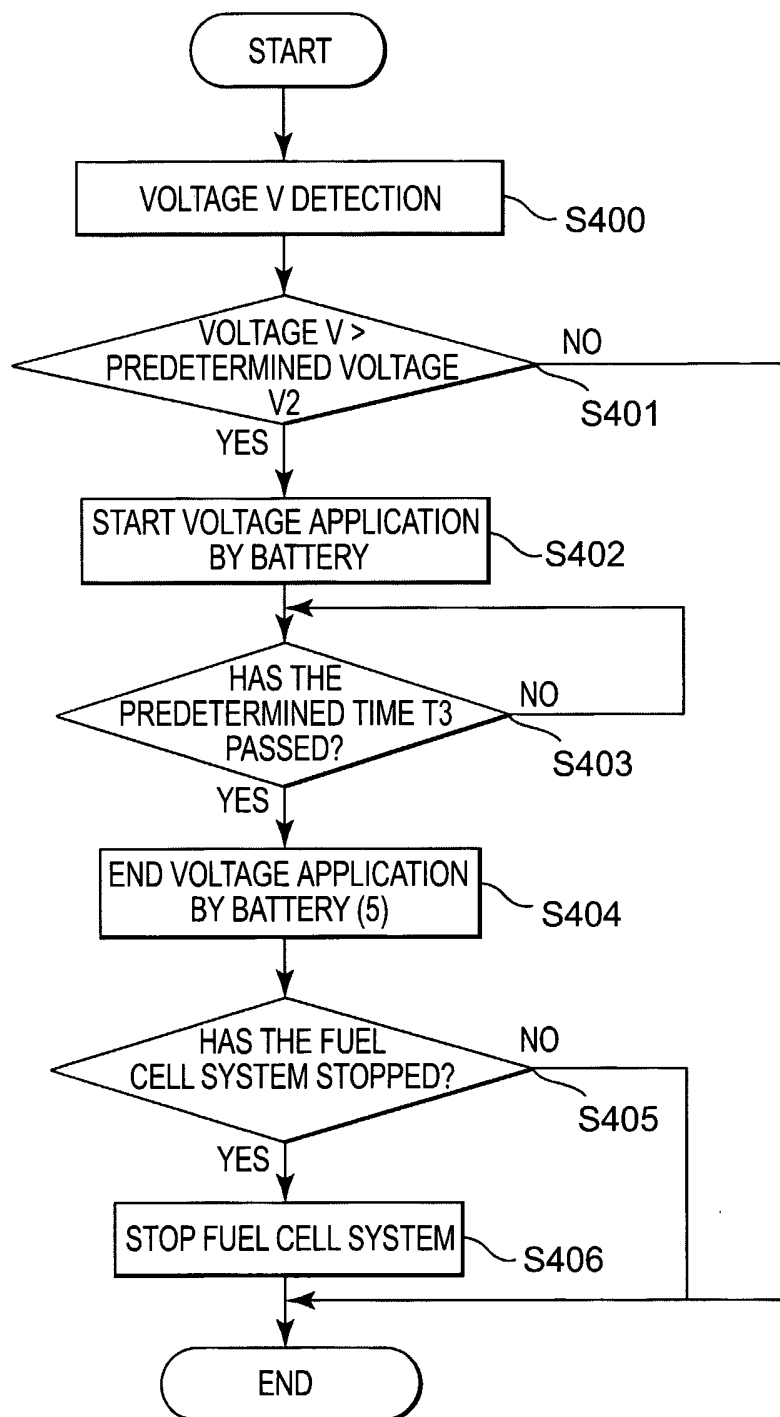
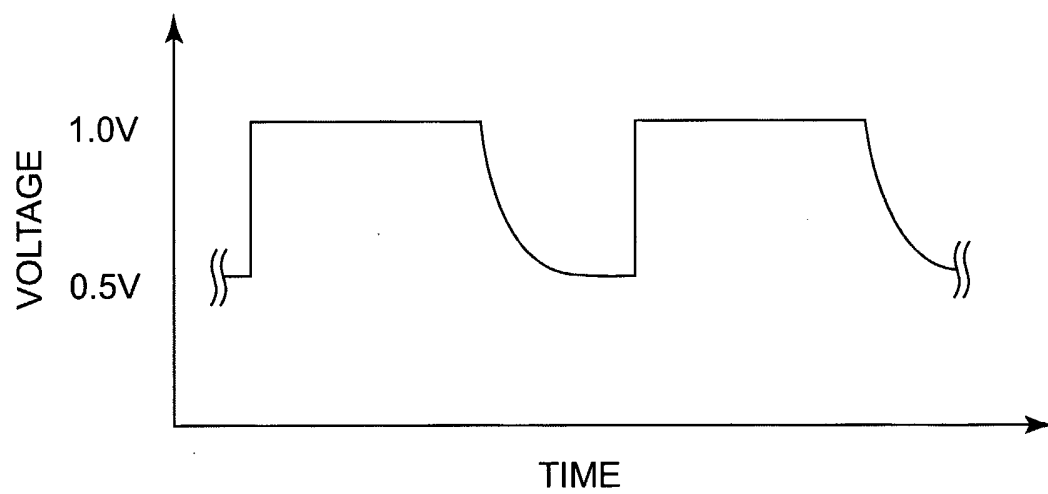


Fig. 11

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**Fig. 12**

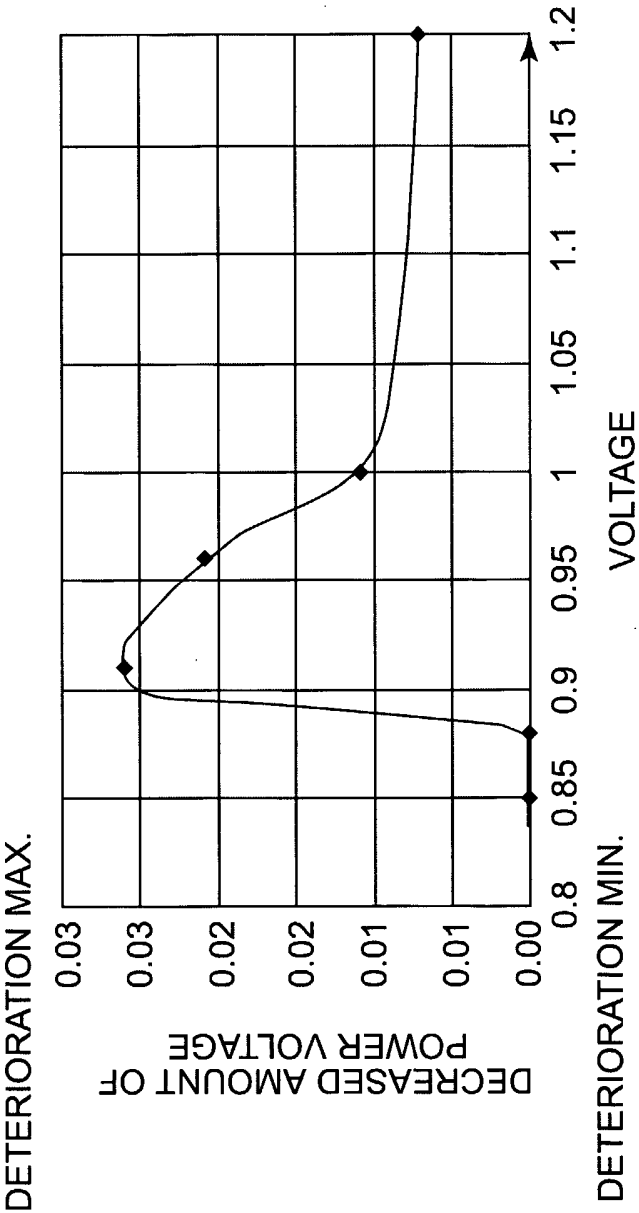


Fig. 13

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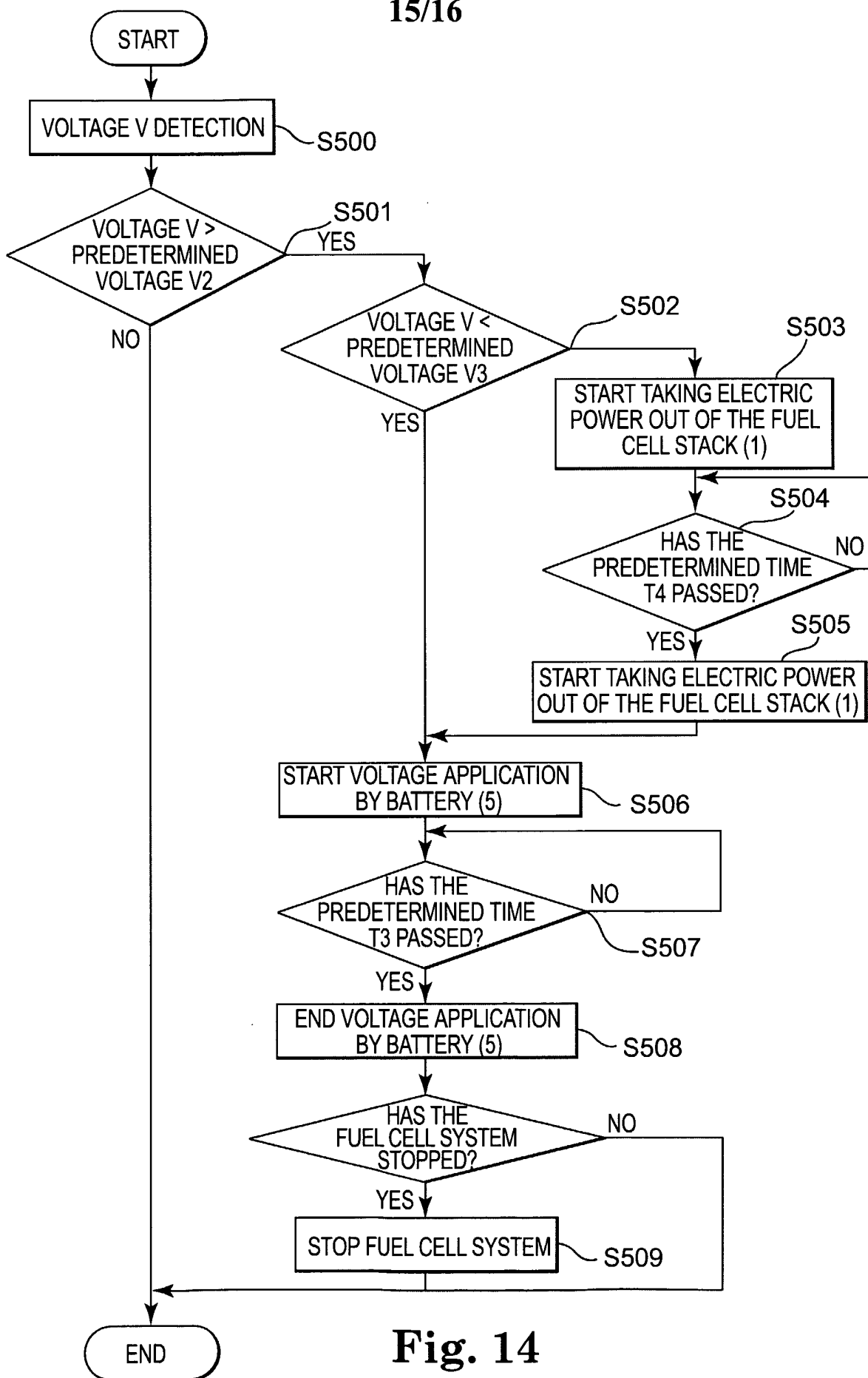
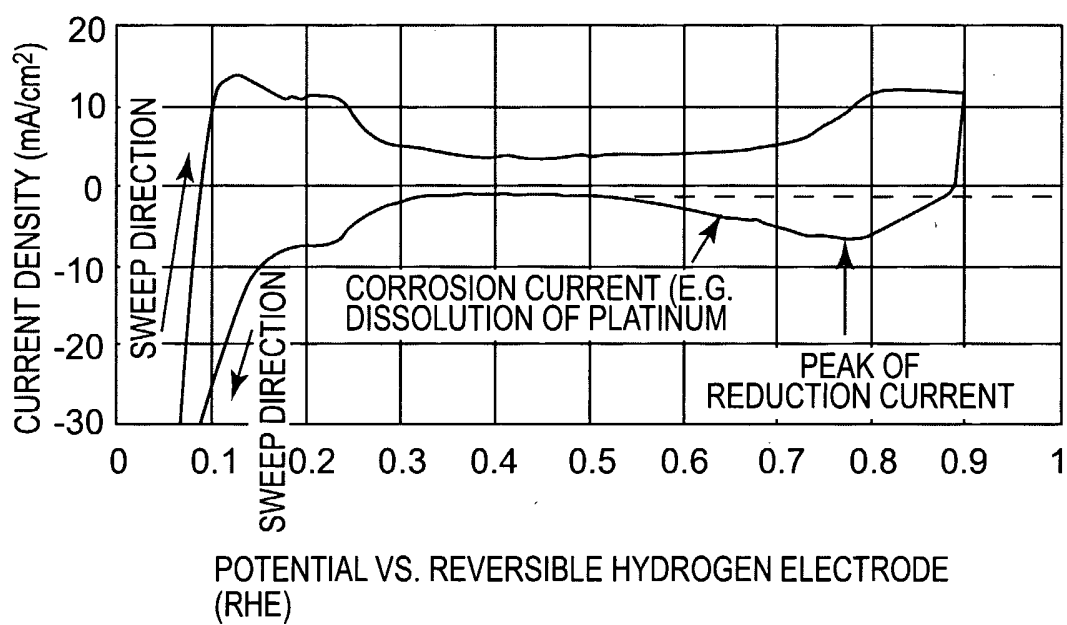


Fig. 14

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**Fig. 15**