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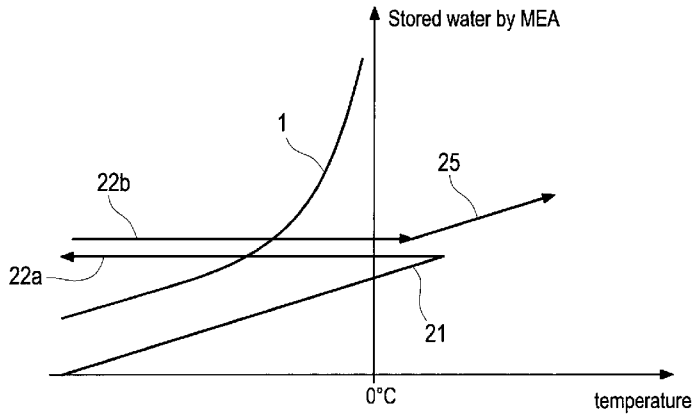


Fig. 3 a

(57) Abstract: Methods are disclosed for starting up a fuel cell system from freezing temperatures below about -15 °C using a two-step procedure involving a single heating phase followed by a single mixing phase. In the heating phase step, a fuel cell stack in the system is operated with essentially no coolant circulation, until the average stack temperature increases above about 15 °C, and preferably higher. In the mixing phase step, operation of the stack is stopped and then, after a predetermined holding time, coolant is circulated. The fuel cell system is essentially started up and ready for normal operation after the mixing phase step. The method is effective and useful for avoiding unacceptable ice formation in the cell components without adversely affecting the stack.

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FREEZE START-UP METHOD FOR FUEL CELL SYSTEM

BACKGROUND

Field of the Invention

This invention relates to improved methods for starting up a fuel cell system at temperatures well below freezing. In particular, it relates to methods for starting up an automotive fuel cell system comprising a solid polymer electrolyte fuel cell stack.

Description of the Related Art

Fuel cells such as solid polymer electrolyte fuel cells electrochemically convert reactants, namely fuel (such as hydrogen) and oxidant (such as oxygen or air), to generate electric power. Solid polymer electrolyte fuel cells generally employ a proton conducting, solid polymer membrane electrolyte between cathode and anode electrodes. A structure comprising a solid polymer membrane electrolyte sandwiched between these two electrodes is known as a membrane electrode assembly (MEA). In a typical fuel cell, flow field plates comprising numerous fluid distribution channels for the reactants are provided on either side of a MEA to distribute fuel and oxidant to the respective electrodes and to remove by-products of the electrochemical reactions taking place within the fuel cell. Water is the primary by-product in a cell operating on hydrogen and air reactants. Because the output voltage of a single cell is of order of 1V, a plurality of cells is usually stacked together in series for commercial applications in order to provide a higher output voltage. Fuel cell stacks can be further connected in arrays of interconnected stacks in series and/or parallel for use in automotive applications and the like.

Along with water, heat is a significant by-product from the electrochemical reactions taking place within a fuel cell. Means for cooling a fuel cell stack is thus generally required. Stacks designed to achieve high power density (e.g. automotive stacks) typically circulate liquid coolant throughout the stack in order to remove heat quickly and efficiently. To accomplish this, coolant flow fields comprising numerous coolant channels are also typically incorporated in the flow field plates of the cells in the stacks. The coolant flow fields may be formed on the electrochemically inactive surfaces of the flow field plates and thus can distribute coolant evenly throughout the cells while keeping the coolant reliably separated from the reactants.

In certain applications, fuel cell stacks may be subjected to repeated on-off duty cycles involving storage for varied lengths of time and at varied temperatures. It is generally desirable to be able to reliably start-up such stacks in a short period of time. Certain applications, like automotive, can require relatively rapid reliable start-up from storage conditions well below freezing. This has posed a significant challenge both because of the relatively low rate capability of cells at such temperatures and also because of problems associated with water management in the cells when operating below 0° C. A certain amount of water is required for proper fuel cell operation (e.g. hydration of the membrane electrolyte) and water is also generated as a result of providing electrical power. However, ice of course forms where liquid water is present at such temperatures. The presence of ice can be problematic depending on how much there is and its location when stored or when starting up. The formation of ice in the electrochemically active MEAs of the fuel cells is particularly problematic during startup from below freezing temperatures.

As a result of the importance of this issue and the difficulties involved, numerous fuel cell designs and start-up methods have been proposed in the art to address the various problems encountered during start-up from temperatures below freezing. For instance, methods have been proposed involving coolant flow switching and/or control (e.g. in JP4823485 and JP5262125).

In other proposals, control of the power drawn from the stack can be involved. For instance, JP2011198653 discusses a method for avoiding undesirably large temperature differences between the coolant inlet and outlet during startup by appropriate use of a power generating controller and coolant pump control.

Other problems encountered during startup can include damage due to thermal shock. In JP 2011175777, a method is disclosed to effectively protect a fuel cell stack against such damage from thermal shock in a sub-zero startup. The method involves repeatedly and alternatively executing a heat operation that generates power while the circulation of the cooling medium is stopped, and a circulation operation that circulates the cooling medium. Numerous such cycles are required to avoid damage from thermal shock, and temperature excursions back to below freezing for the fuel cell stack are avoided.

Despite the advances made to date, there remains a need for simpler and effective methods for starting up fuel cell systems from subzero temperature. This invention represents an option for fulfilling these needs and provides further related advantages.

SUMMARY

The present invention relates to starting up a fuel cell system in which the system comprises a fuel cell stack, a coolant circuit configured to circulate coolant through the fuel cell stack, and an electrical load. Further, the invention comprises a method for starting up the fuel cell system from temperatures well below freezing, i.e. from a starting temperature T_{start} below about -15 °C. The method consists essentially of a single heating phase step followed by a single mixing phase step whereby the fuel cell system is started up after the mixing phase step.

Specifically, the heating phase step comprises supplying fuel and oxidant reactant gases to the fuel cell stack, and connecting the electrical load to the fuel cell stack thereby drawing power from the fuel cell stack. However, during the heating phase step, there is essentially no circulation of coolant through the coolant circuit. The heating phase step continues until the temperature of the fuel cell stack increases above about 15 °C and preferably to higher values. In exemplary embodiments for instance, the heating phase step continues until the fuel cell stack reaches a temperature between about 30 and about 60 °C.

The mixing phase step comprises the steps of disconnecting the electrical load such that essentially no power is drawn from the fuel cell stack, waiting an optional predetermined holding time after disconnecting the electrical load, starting to circulate coolant through the coolant circuit after the predetermined holding time, and continuing to circulate coolant through the coolant circuit for a mixing phase time. The mixing phase step ends after the mixing phase time.

The method can be effective if the temperature of the fuel cell system (including at least the fuel cell stack and coolant circuit) after the mixing phase time ends up being greater than 0 °C. In the following, if the fuel cell stack has a thermal capacity C_{stack}, the coolant circuit has a thermal capacity $C_{cooling}$, and the temperature of the fuel cell stack at the end of the heating phase step is denoted $T_{heating}$, the method can generally be effective if the heating phase step is continued until the temperature of the fuel cell stack increases such that $T_{heating}$ is greater than the product of $|T_{start}|$ times $C_{cooling}$ divided by C_{stack}. For instance, in a situation where $C_{cooling}$ is greater than or about 2 times C_{stack}, the method can be effective when starting up from -15 °C if the heating phase step continues until the fuel cell stack reaches a temperature above 30 °C.

In an exemplary embodiment, the fuel cell system additionally comprises high voltage circuitry and a contactor that switchably connects the fuel cell stack to the high voltage circuitry. The method can then

further comprise opening the contactor during the mixing phase step, and closing the contactor after the mixing phase step. In particular, the contactor may be closed if the open circuit voltage of the fuel cell stack is below an upper voltage limit for the high voltage circuitry. Further, a load resistor may be applied across the fuel cell stack after closing the contactor if the open circuit voltage of the fuel cell stack is above an upper voltage limit for the high voltage circuitry.

During the heating phase step, in some embodiments it may be advantageous to monitor the pressure drop of the oxidant reactant gas within the fuel cell stack, and control the flow rate of the oxidant reactant gas such that the pressure drop is less than a predetermined pressure value. Alternatively, it may be advantageous to determine the temperature of the fuel cell stack at an inlet, at an outlet, and in the middle, and control the flow rate of the oxidant reactant gas based on the relative magnitudes of the temperature at the inlet, the temperature at the outlet, and the temperature in the middle.

In the mixing phase step, the predetermined holding time for certain embodiments can range from 0 to 120 seconds. The end of the mixing phase step (and hence length of the mixing phase time) may be based on a variety of different conditions. For instance, the mixing phase time itself can be predetermined. Alternatively, the method can comprise the step of monitoring the impedance of the fuel cell stack, and the end of the mixing phase step can depend on when the monitored impedance decreases to a predetermined impedance value. Further still, the method can comprise the steps of monitoring the temperature of the fuel cell stack at an inlet and an outlet, and determining an average monitored temperature from the monitored inlet and outlet temperatures, and then the end of the mixing phase step can depend on when the average monitored temperature has equilibrated to a predetermined temperature greater than 0 °C.

During the mixing phase step, in some embodiments it may be advantageous to set the flow rate of the oxidant reactant gas at a maximum value at the start of the mixing phase step, to monitor the temperature of the fuel cell stack, and to controllably reduce the flow rate of the oxidant reactant gas according to a decrease in the monitored temperature of the fuel cell stack.

The method of the invention is generally suitable for use in systems comprising solid polymer electrolyte fuel cell stacks. Hence the invention also includes fuel cell systems configured to operate according to such a method. And the invention is particularly suitable for use in automotive fuel cell systems.

These and other aspects of the invention are evident upon reference to the attached Figures and following detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 plots the sum of the water initially present plus water generated in the MEA versus MEA temperature and qualitatively illustrates desirable and undesirable regions for operating a fuel cell stack for an automotive fuel cell system at sub-zero temperatures.

Figures 2a, 2b and 2c qualitatively illustrate prior art start-up situations comprising one or more heating phases. The situations in Figures 2b and 2c also comprise a single and multiple mixing phases respectively.

Figures 3a and 3b illustrate the improved situation for starting up an automotive fuel cell system at temperatures well below freezing using methods of the invention. The methods in Figures 3a and 3b employ zero and non-zero predetermined holding times respectively during the mixing phase step.

Figure 4 is a schematic of an exemplary automotive fuel cell system which can be started up from a temperature well below freezing using the method of the invention.

DETAILED DESCRIPTION

In this specification, words such as "a" and "comprises" are to be construed in an open-ended sense and are to be considered as meaning at least one but not limited to just one.

Herein, in a quantitative context, the term "about" should be construed as being in the range up to plus 10% and down to minus 10%.

Methods and associated systems have been developed for improved startup of fuel cell systems from temperatures well below freezing, e.g. from temperatures below -15 °C. During the heating phase step, enough water may get generated such that during the subsequent mixing phase step it becomes temporarily frozen in the active cell components to be unacceptable for subsequent operation. However, by the end of the mixing phase step, this water will have melted and thus subsequent acceptable operation is possible.

To start up a fuel cell at very low temperatures, a specific electrical load is connected across the fuel cell and the fuel cell is operated thereby generating a controlled amount of heat for heating itself up. As always, water is generated at the cathode in the MEA during operation. Some of the generated water is removed, mainly as vapour, by the flowing reactant gases. But if sufficient liquid water accumulates and freezes in the pores in the cathode structure, the pores may effectively become filled with ice, blocking the flow of reactant and product gases therein, and thus prevent the fuel cell from generating any significant power. In fact, this is generally what happens when starting up a fuel cell from very low temperatures if too much water is generated too quickly. And once this happens, it can take a relatively long time to complete start-up. It is therefore desirable to avoid operating the fuel cell in regimes where this can occur.

Figure 1 qualitatively illustrates desirable and undesirable regions for operating a fuel cell stack for an automotive fuel cell system at sub-zero temperatures. The X-axis of the graph in Figure 1 shows MEA temperature and the Y-axis shows the combined total of the water initially present in the MEA plus the water generated in the MEA. During start-up, the total water potentially present in the MEA over time is a combination of the water initially present before start-up begins plus the water generated during subsequent operation. This latter amount is a direct function of the total charge generated by operation of the fuel cell. While water is generated over time as a result of fuel cell operation, water is also removed over time in the exhaust gases from the cathode and anode. Water is removed relatively easily if in a vapour state and to some extent if in a liquid state, but it is removed only very slowly once frozen. In addition, a certain amount of the water generated in the MEA may transfer to and reside in the gas diffusion layers instead of in the channels in the plate. Curve 1 represents the amount of water which can remain in the MEA as a function of temperature before the fuel cell actually becomes incapable of providing any significant power. Curve 1 has been determined experimentally by mapping the charge generated and temperature values where the power capability of conventional fuel cells drops off markedly during operation. The region above curve 1 represents an undesirable region for operation. In this region, sufficient water has remained and has frozen in the MEA so as to block the cathode pores and limit power production. On the other hand, the region below curve 1 represents a desirable region for operation. In this region, the water which may remain in the MEA is insufficient to block the cathode pores and limit power production. Curve 1 therefore represents what is referred to herein as an ice tolerance curve.

Dashed curve 2 represents the calculated static capacity for water in the MEA as a function of temperature. The static capacity for water includes the pore volume in the cathode (which is essentially constant as a function of temperature) and also the water uptake capability of the ionomer membrane and ionomer in the electrodes. The water uptake capability of the ionomer increases as a function of temperature and thus curve 2 has a positive slope. Calculated curve 2 thus also represents a capacity for ice to form before the cathode pores become blocked and limit further power generation. Curve 2 closely follows curve 1 from very low temperatures up to about -15 °C and thus calculation matches actual behaviour over this range of temperatures. Above about -15 °C though, the two curves diverge significantly. Surprisingly, there is a region 3 (shown hatched in Figure 1) of significant size between curves 1 and 2 over the temperature range from about -15 °C to 0 °C. It has been found that fuel cells can operate in this region, temporarily at least, without suffering complete ice blockage and thus losing power. Clearly enough water would have been generated for this to happen in principle, if that water had frozen and remained in the cell. It has also been found that if a fuel cell remains in a state in region 3 for a long enough period of time, power production drops markedly as if the pores were blocked with ice. The time it takes for this to occur ranges from seconds to minutes depending on how close the MEA temperature is to the freezing point.

It is believed that this phenomena arises from water being in a supercooled state in region 3. As discussed in more detail in "Ice-Crystallization Kinetics and Water Movement in Gas-Diffusion and Catalyst Layers", T. J. Dursch et al., ECS Transactions, 50 (2) 429-435 (2012), in the MEA of a fuel cell, there can be a marked inflection in the rate of water crystallization at around -15 °C. Consequently, the water can exist in a supercooled state in region 3 and remain liquid for short periods of time.

For comparison, several prior art start-up situations are qualitatively illustrated in the plots of Figures 2a-2c, while start-ups using methods of the invention are illustrated in Figures 3a and 3b. The plots in all these figures show the same axes and ice tolerance curve 1 as shown in Figure 1. Also, in all these illustrated start-up methods, the fuel cell stack is initially operated with no coolant flowing therethrough. This allows for as much of the generated heat as possible to go to the fuel cell stack itself, rather than to the coolant and associated coolant subsystem.

In one start-up scenario in the prior art, an electrical load is applied across the fuel cell stack and power is drawn with coolant circulating through the coolant circuit. Heat and water are generated in the MEAs in the stack and this heat is distributed throughout both the fuel cell stack and the coolant circuit. Prior art curve 10 in Figure 2a illustrates the temperature state of the MEAs in this scenario. Henceforth curve 10

will be referred to as heating phase curve 10. As qualitatively shown in Figure 2a, heating phase curve 10 enters the region above ice tolerance curve 1. The water in the MEAs freezes in a sufficient amount to drastically limit power production (as depicted with a * in Figure 2a). To avoid that from happening, in an alternative start-up scenario in the prior art, coolant is not circulated through the coolant circuit during the initial start-up process. In this situation, the heat generated from stack operation is not distributed to the coolant circuit. With a smaller thermal capacity involved now, the state of the MEAs follows a curve more like heating phase curve 11, never entering the region above ice tolerance curve 1, until the resultant fuel cell stack temperature is well above freezing. Up to this point at least, this approach avoids forming an unacceptable amount of ice in the MEAs.

Once the fuel cell stack itself has been heated up successfully though, the coolant and coolant subsystem also need to be brought up to operating temperature. However, in typical automotive embodiments, if the coolant subsystem is simply turned on, the heat capacity of the sub-zero coolant and associated subsystem are sufficient to cool the fuel cell stack to sub-zero temperatures again. In some fuel cell embodiments, the thermal shock associated with such a large, rapid change to subzero temperatures alone can cause damage to the fuel cell stack. And further, because the coolant circuit is designed to make intimate thermal contact with the MEAs in the stack, the MEAs also are cooled to sub-zero temperatures again. The water therein freezes with sufficient ice forming in the MEAs to block reactant access and limit further power production. In addition, as the fuel cell stack continues to operate during this period, additional water is generated, thus making matters even worse. This situation is illustrated in Figure 2b. As represented here, the coolant subsystem is turned on and coolant starts to circulate at the end of heating phase curve 11. The MEA temperature drops as cold coolant circulates throughout the stack while water continues to be generated. The state of the MEAs now follows prior art curve 12, which will henceforth be referred to as mixing phase curve 12 (to represent the mixing of the coolant throughout the fuel cell system during this period). As illustrated in Figure 2b, the MEA can enter the region above ice tolerance curve 1 with the consequence that sufficient ice forms in the MEA to limit power production (again denoted with a * in Figure 2b).

A prior art method for avoiding these negative outcomes is illustrated in Figure 2c. Here, a method disclosed in the aforementioned JP 2011175777 is illustrated in a format similar to those used in Figures 1-2b. Initially, the fuel cell is operated with no coolant flowing as represented by heating phase curve 11a. At the end of heating phase curve 11a, the electrical load is removed and power ceases to be drawn from the fuel cell stack. Thus advantageously no further water is generated for now. Again, the flow of coolant is started, thereby starting to heat the coolant but also cooling the stack and MEAs therein. The

coolant flow is then stopped, and once again the electrical load is applied and power drawn from the fuel cell stack. The state of the MEAs thus follows mixing phase curve 12a when the coolant is circulating and then follows heating phase curve 11b once the flow of coolant is again stopped. This process is repeated multiple times at sub-zero temperatures after which the fuel cell stack is now ready for normal use. This process is depicted in Figure 2c using another mixing phase curve 12b, then another heating phase curve 11c, and finally another mixing phase curve 12c. At this point, the fuel cell stack is ready for normal use and a wide range of electrical loads can be applied to the fuel cell stack without problem. In an automotive application, the automobile is thus essentially ready to drive. And in Figure 2c, the state of the MEA once normal operation has begun is illustrated as driving phase curve 15.

The present invention takes advantage of the ability of certain fuel cell constructions (e.g. those employing soft elastomer seals) to handle the thermal shock associated with large, rapid temperature transitions from above to below zero temperature. In addition, it takes advantage of the typical thermal capacities of the stack and coolant circuits encountered in certain fuel cell applications (e.g. automotive) along with the ability to heat the fuel cell stack up to temperatures well above ambient without damage. Figures 3a and 3b qualitatively illustrate start-ups of an automotive fuel cell stack from temperatures well below freezing using methods of the invention. The methods in Figures 3a and 3b differ in that they employ zero and non-zero predetermined holding times respectively during the mixing phase step.

In Figure 3a, as before the fuel cell stack initially operates with no coolant flowing as represented by heating phase curve 21. At the end of heating phase curve 21, the electrical load is removed and power ceases to be drawn from the fuel cell stack. Again advantageously no further water is generated for now. The flow of coolant is now started, thereby heating the coolant and cooling the MEAs. Here, the coolant flow continues even though the temperature of the MEAs falls below zero. This step is represented by mixing phase curves 22a and 22b. Due to the intimate thermal contact between the MEAs and the coolant circuit, initially the MEA temperature quickly falls, albeit temporarily, essentially back to the original starting temperature. This is illustrated by initial mixing phase curve 22a.

While some of the water generated in the MEA during the heating phase step may have been removed as vapour or moved to an adjacent gas channel, there is still a substantial amount of water present in the MEA. As a result of the temporary drop in temperature illustrated by mixing phase curve 22a, this water in the MEA freezes and temporarily blocks pores in the MEA. However, as the mixing phase step continues, the heat associated with the hotter fuel cell stack is distributed to the colder coolant circuit. As the temperature of the fuel cell stack equilibrates with that of the coolant circuit, the MEA temperature

rises again as illustrated in final mixing phase curve 22b. If the temperature of the equilibrated fuel cell stack and coolant circuit is above freezing as shown in Figure 3a, the frozen water in the MEAs will have melted. Thus, the stack can be operated normally at this point as represented by driving phase curve 25.

In order that the temperature of the fuel cell stack and coolant circuit ends up above 0 °C at the end of the mixing phase step (i.e. the end of mixing phase curve 22b), the fuel cell stack has to have been heated sufficiently at the end of the heating phase step such that there is enough heat available to have heated up the coolant circuit sufficiently once equilibrated. This can be achieved if the fuel stack temperature $T_{heating}$ at the end of the heating phase step is greater than the product of $|T_{start}|$ times $C_{cooling}$ divided by C_{stack} (where T_{start} is the starting temperature, C_{stack} is the thermal capacity of the fuel cell stack and $C_{cooling}$ is the thermal capacity of the coolant circuit). Importantly, because no power is drawn from the fuel cell stack during the mixing phase step, no additional water is generated which would have to be heated and which could cause complications as the system temperature equilibrates.

In fuel cell systems intended for certain applications, such as automotive applications, the typical thermal capacities of the fuel cell stack and coolant circuit are such that the required fuel stack temperatures $T_{heating}$ to accomplish such a start-up are well within an acceptable level for operation (i.e. do not damage the fuel cell stack). For instance, in an exemplary automotive fuel cell stack, C_{stack} may be about half that of $C_{cooling}$. Thus, when starting up such a system from -15 °C, the fuel cell stack would need to be heated to a $T_{heating}$ of greater than about 30 °C during the heating phase step in order to obtain a result like that qualitatively shown in Figure 3a. In a like manner, when starting up such a system from -30 °C, the fuel cell stack would need to be heated to a $T_{heating}$ of greater than about 60 °C during the heating phase step. Of course, typical solid polymer electrolyte fuel cell stacks can readily tolerate such temperatures and may routinely operate at temperatures up to 90 °C.

The method shown in Figure 3a is thus simpler than that depicted in Figure 2c and thus represents an improved method for starting-up an automobile from temperatures well below freezing.

The method illustrated in Figure 3b is similar to that shown in Figure 3a, except that the flow of coolant is not started immediately at the end of heating phase 21. Instead, the procedure involves waiting a predetermined holding time before starting the flow of coolant. The mixing phase curve here thus comprises predetermined holding time portion 30 along with portions 32a and 32b in which coolant circulates through the coolant subsystem. During the predetermined holding time, water is removed to some extent from the MEAs (as discussed before). As a result, the MEA state at the end of the mixing

phase step here is advantageously further away from the ice tolerance curve limit than the equivalent MEA state at the end of the mixing phase step of Figure 3a. The method illustrated in Figure 3b can thus avoid ice blockages with greater certainty than the method of Figure 3a, without significantly extending the start-up time overall.

Figure 4 shows a schematic of an exemplary automotive fuel cell system that is configured to operate according to this improved method. Fuel cell system 101 comprises solid polymer electrolyte fuel cell stack 102 which is supplied with fuel (hydrogen) reactant at fuel inlet 103 and oxidant (air) reactant at oxidant inlet 104. The exhaust fluids from the stack anodes and cathodes exit the stack at fuel outlet 105 and oxidant outlet 106 respectively. A series of temperature sensors is depicted in this exemplary embodiment in order to monitor the temperature of the stack at several locations. These include temperature monitoring sensors 107, 108, and 109 which are located at fuel inlet 103, the middle of the stack, and fuel outlet 105 respectively. Further, oxidant flow rate control 110 is provided in the oxidant line leading to oxidant inlet 104. And, differential pressure monitor 111 is provided in the oxidant line leading out from oxidant outlet 106. Differential pressure monitor 111 is configured to measure the pressure difference between the oxidant supply at inlet 104 and the oxidant exhaust at outlet 106. (Optionally, but not shown in Figure 4, two pressure sensors may be employed at inlet 104 and outlet 106 respectively.)

Fuel cell system 101 also includes a coolant subsystem to control stack temperature. In this subsystem, coolant is obtained from the stack at coolant outlet 113, is circulated through radiator 112, and then returned to the stack at coolant inlet 114.

Figure 4 also shows several circuits connected across the positive and negative terminals 115, 116 of the fuel cell stack. In this exemplary embodiment, impedance monitor 117 is connected across the terminal for purposes of measuring stack impedance. Fuel cell system 101 also comprises certain high voltage circuitry 118 (e.g. traction motor, DC-DC converter, and the like) which can be connected to or disconnected from the stack terminals using contactor 119. Further, fuel cell system 101 comprises electrical load 120 which is of appropriate size for purposes of cold start-up and which is switchably connected across terminals 115 and 116 using switch 121. The vehicle itself comprises drive motor and other peripherals (not shown) which can be connected across the fuel cell stack terminals once start-up is complete. (It should be noted that while high voltage circuitry 118 and electrical load 120 are depicted as distinct from each other as well as from the vehicle drive motor and other peripherals, it may be possible to employ certain components and/or portions of circuitry 118, or alternatively the motor and/or other

peripherals, to serve as electrical load 120. Any such possibility would be dependent on the specifics of the vehicle construction and operation, and it is expected that those skilled in the art would appreciate what might be done in this regard.)

In starting up fuel cell system 101 from sub-zero temperatures, first a heating phase step is employed. Fuel and oxidant reactant gases are supplied to inlets 103 and 104 respectively and appropriately sized electrical load 120 is connected across stack terminals 115, 116 by closing switch 121. During the heating phase, there is essentially no circulation of coolant through radiator 112 and the associated coolant line.

During the heating phase, it may be advantageous to control the flow rate of the oxidant reactant gas such that the pressure drop through the cathodes in the stack does not increase unduly (i.e. is controlled to be less than a predetermined pressure value). Instability and/or a significant rise in this pressure drop may be indicative of too much or uneven water distribution in the stack. In such a case, the oxidant flow rate may desirably be reduced to avoid ice blockages. Differential pressure monitor 111 may be used to monitor the pressure drop of the oxidant reactant gas within the fuel cell stack, and oxidant flow rate control 110 may be used to control the flow rate accordingly.

It may also be advantageous during the heating phase to check for a significant uneven temperature distribution over the stack. Again, this can be indicative of undesirable water amounts or distribution in the stack. In such a case, it can again be desirable to control (reduce) the flow rate of a reactant gas or gases to avoid ice blockages. In this exemplary embodiment, temperature sensors 107, 108, 109 which are located at inlet 103, middle of stack 102, and outlet 105 may be used to monitor for uneven temperature distribution over stack 102. If the temperature in the middle of the stack is, for instance, well above freezing, yet the temperatures at inlet 103 and outlet 105 are still below freezing, the flow of oxidant can then desirably be reduced using oxidant flow rate control 110. On the other hand, the flow of oxidant can desirably be increased if all the measured temperatures are similar and below freezing.

In typical embodiments, the heating phase step continues until the temperature of the fuel cell stack increases substantially, e.g. to be in the range between about 30 and 60 °C. After the heating phase step has been completed, the mixing phase step begins. Electrical load 120 is disconnected by opening switch 121 such that essentially no power is drawn from the fuel cell stack. Optionally, there may then be a waiting period for a predetermined holding time (e.g. 0 to 120 seconds) before starting to circulate coolant. At the end of the predetermined holding time, circulation of the coolant is started and continues

for a mixing phase time. After the mixing phase time, the mixing phase step has ended and the fuel cell system has essentially been started up. The fuel cell system is now ready to operate normally and the automobile can now be driven.

Because the fuel cell stack is essentially under no load during the mixing phase step, the open circuit voltage of the stack may potentially rise to values that threaten high voltage circuitry 118 (i.e. an upper voltage limit therefor). To protect against this, contactor 119 may be opened during the mixing phase step and closed after the mixing phase step. If the open circuit voltage of the stack is sufficiently low however, contactor 119 may be closed. Also note that when the contactor is closed at the end of the mixing phase step, a load resistor (not shown in Figure 4) may be used to drop the voltage across the stack if the open circuit voltage of the stack is still too high to threaten high voltage circuitry 118.

The end of the mixing phase (i.e. a suitable mixing phase time) can be based on a predetermined time or based on average monitored temperature or fuel cell impedance. For instance, the impedance of the stack may be monitored via impedance monitor 117 and the mixing phase step ended when the monitored impedance decreases to a predetermined impedance value. Alternatively, the temperature of the fuel cell stack may be monitored at inlet (e.g. inlet 103) and an outlet (e.g. 105), an average monitored temperature determined from these two monitored temperatures, and the mixing phase step ended when the average monitored temperature decreases to a predetermined temperature greater than 0 °C.

In a like manner to controlling the flow of oxidant reactant gas during the heating phase step, it may be advantageous to do the same during the mixing phase step. In order to better remove water, the reactant gas flows may be set at maximum when the stack is above freezing but reduced once the stack temperature falls below zero again to avoid the possibility of ice formation and blockages. Specifically then, the flow rate of the oxidant reactant gas may be set at a maximum value using oxidant flow rate control 110 at the start of the mixing phase step, and the temperature of the fuel cell stack monitored using any or all of temperature sensors 107, 108, 109. Then, the flow rate of the oxidant reactant gas may be controllably reduced, again using oxidant flow rate control 110, according to a decrease in the monitored temperature of the fuel cell stack.

All of the above U.S. patents, U.S. patent applications, foreign patents, foreign patent applications and non-patent publications referred to in this specification, are incorporated herein by reference in their entirety.

While particular elements, embodiments and applications of the present invention have been shown and described, it will be understood, of course, that the invention is not limited thereto since modifications may be made by those skilled in the art without departing from the spirit and scope of the present disclosure, particularly in light of the foregoing teachings. For instance, while the preceding description was mainly directed at liquid cooled fuel cell systems, it is possible to consider using the disclosed methods for air cooled or other fuel cell systems as well. Such modifications are to be considered within the purview and scope of the claims appended hereto.

What is claimed is:

1. A method for starting up a fuel cell system from a starting temperature T_{start} below about -15 °C, the fuel cell system comprising a fuel cell stack, a coolant circuit configured to circulate coolant through the fuel cell stack, and an electrical load; the method consisting essentially of:

a heating phase step comprising:

supplying fuel and oxidant reactant gases to the fuel cell stack; and

connecting the electrical load to the fuel cell stack thereby drawing power from the fuel cell stack; and

continuing the heating phase step until the temperature of the fuel cell stack increases above about 15 °C;

wherein there is essentially no circulation of coolant through the coolant circuit during the heating phase step;

and

a mixing phase step comprising:

disconnecting the electrical load such that essentially no power is drawn from the fuel cell stack;

waiting a predetermined holding time after disconnecting the electrical load;

starting to circulate coolant through the coolant circuit after the predetermined holding time;

continuing to circulate coolant through the coolant circuit for a mixing phase time; and

ending the mixing phase step after the mixing phase time;

whereby the fuel cell system is started up after the mixing phase step.

2. The method of claim 1 wherein the fuel cell stack has a thermal capacity C_{stack}, the coolant circuit has a thermal capacity $C_{cooling}$, and the temperature of the fuel cell stack at the end of the heating phase step is $T_{heating}$, and the method comprises:

continuing the heating phase step until the temperature of the fuel cell stack increases such that:

$$Theating > \frac{(|Tstart| * Ccooling)}{Cstack}$$

3. The method of claim 1 comprising continuing the heating phase step until the temperature of the fuel cell stack increases to be in the range between about 30 and 60 °C.

4. The method of claim 2 wherein $C_{cooling}$ is greater than or about 2 times C_{stack}.

5. The method of claim 2 wherein the temperature of the fuel cell system after the mixing phase time is greater than 0 °C.

6. The method of claim 1 wherein the fuel cell system additionally comprises high voltage circuitry and a contactor that switchably connects the fuel cell stack to the high voltage circuitry, and wherein the method comprises:

opening the contactor during the mixing phase step; and

closing the contactor after the mixing phase step.

7. The method of claim 6 comprising closing the contactor during the mixing phase step if the open circuit voltage of the fuel cell stack is below an upper voltage limit for the high voltage circuitry.

8. The method of claim 6 comprising applying a load resistor across the fuel cell stack after closing the contactor if the open circuit voltage of the fuel cell stack is above an upper voltage limit for the high voltage circuitry.

9. The method of claim 1 wherein the heating phase step comprises:

monitoring the pressure drop of the oxidant reactant gas within the fuel cell stack; and

controlling the flow rate of the oxidant reactant gas such that the pressure drop is less than a predetermined pressure value.

10. The method of claim 1 wherein the heating phase step comprises:

determining the temperature of the fuel cell stack at an inlet, at an outlet, and in the middle; and

controlling the flow rate of the oxidant reactant gas based on the relative magnitudes of the temperature at the inlet, the temperature at the outlet, and the temperature in the middle.

11. The method of claim 1 wherein the predetermined holding time ranges from 0 to 120 seconds.

12. The method of claim 1 wherein the mixing phase time is predetermined.

13. The method of claim 1 comprising:

monitoring the impedance of the fuel cell stack; and

ending the mixing phase step when the monitored impedance decreases to a predetermined impedance value.

14. The method of claim 1 comprising:

monitoring the temperature of the fuel cell stack at an inlet and an outlet;

determining an average monitored temperature from the monitored inlet and outlet temperatures; and

ending the mixing phase step when the average monitored temperature has equilibrated to a predetermined temperature greater than 0 °C.

15. The method of claim 1 wherein the mixing phase step comprises:

setting the flow rate of the oxidant reactant gas at a maximum value at the start of the mixing phase step;

monitoring the temperature of the fuel cell stack; and

controllably reducing the flow rate of the oxidant reactant gas according to a decrease in the monitored temperature of the fuel cell stack.

16. The method of claim 1 wherein the fuel cell stack in the fuel cell system is a solid polymer electrolyte fuel cell stack.

17. The method of claim 16 wherein the fuel cell system is an automotive fuel cell system.

18. A fuel cell system comprising:

a fuel cell stack;

a coolant circuit configured to circulate coolant through the fuel cell stack; and

an electrical load;

wherein the fuel cell system is configured to operate according to the method of claim 1.

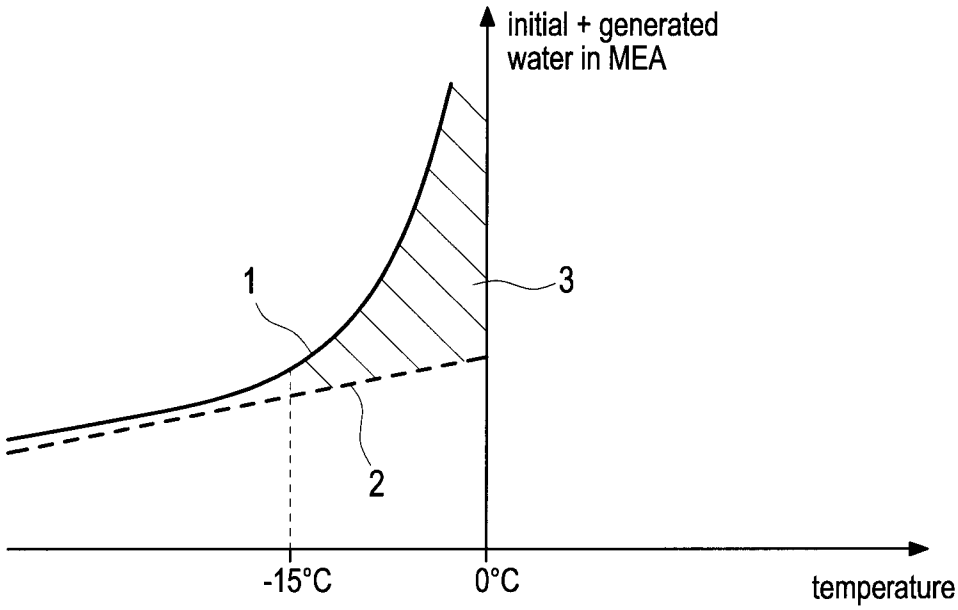


Fig. 1

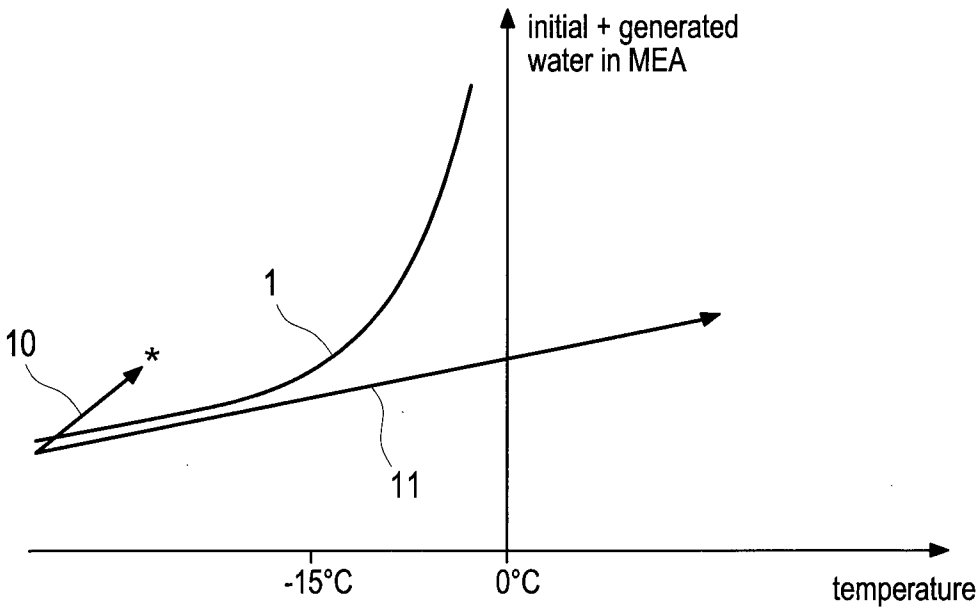


Fig. 2 a
(Prior art)

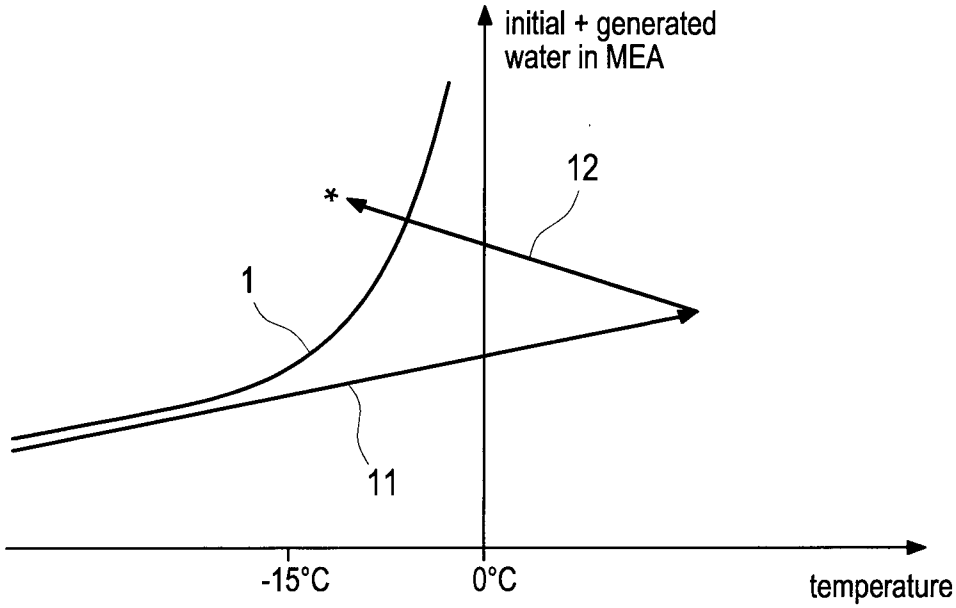


Fig. 2 b
(Prior art)

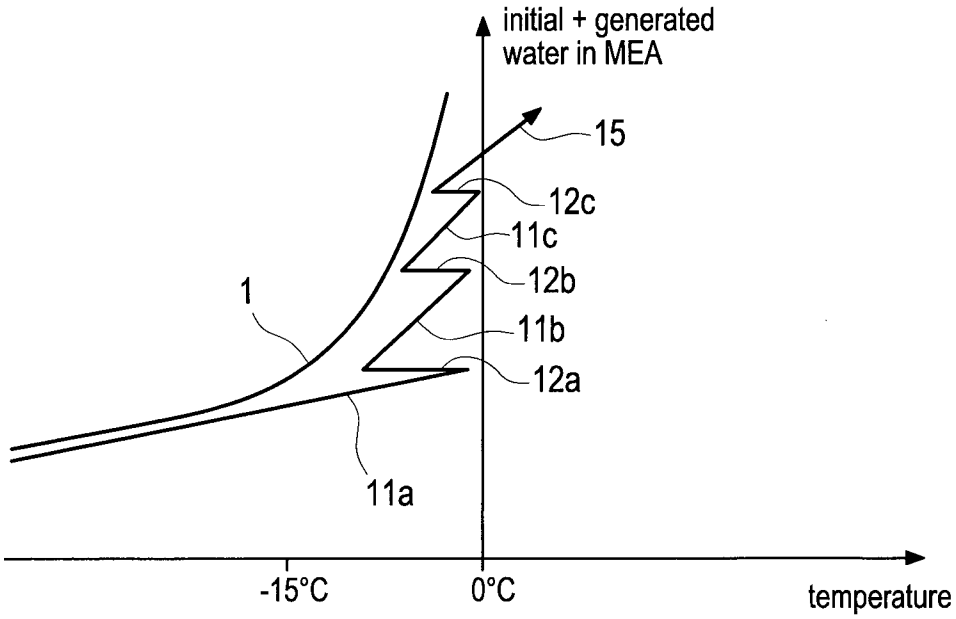


Fig. 2 c
(Prior art)

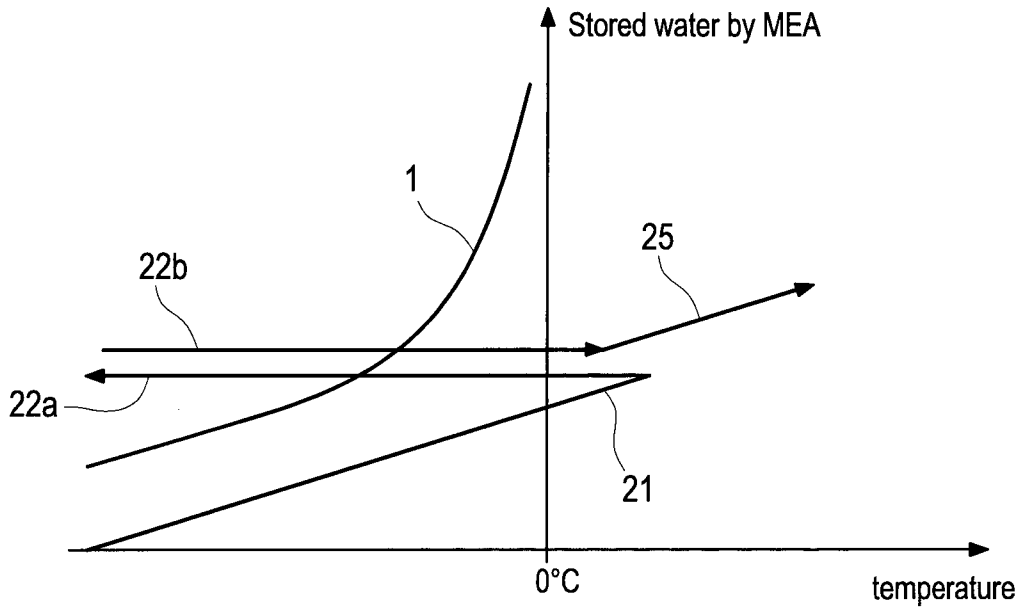

Stored water by MEA
1
25
22b
22a
21
0°C
temperature

Fig. 3 a

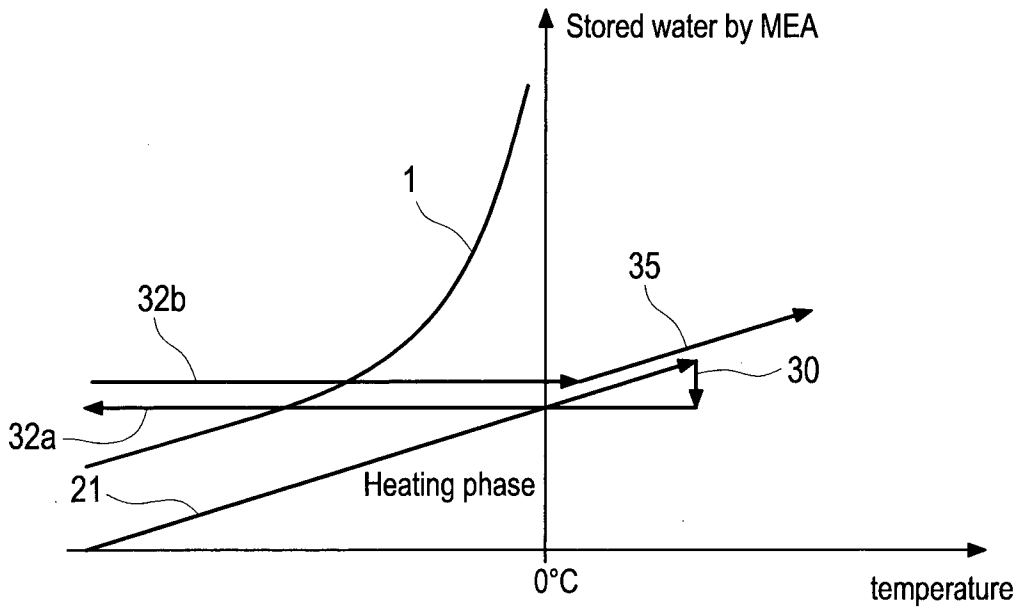

Stored water by MEA
1
35
32b
30
32a
21
Heating phase
0°C
temperature

Fig. 3 b

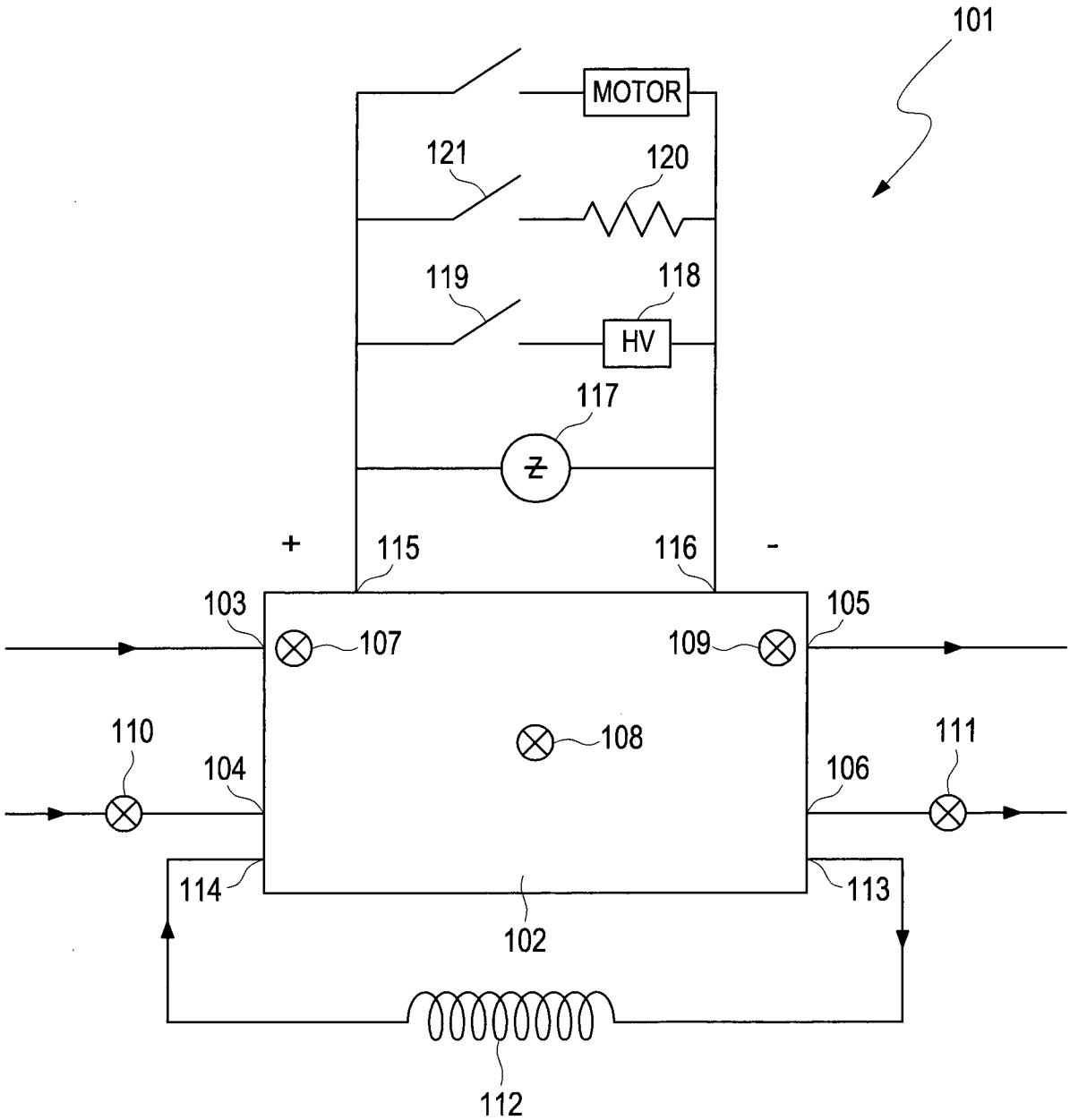

101
MOTOR
121
120
119
118
HV
117
+
115
116
-
103
105
107
109
110
108
111
104
106
114
113
102
112

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2016/000893

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M8/04828 H01M8/0432 H01M8/04537 H01M8/04746 H01M8/04302
ADD. H01M8/1018

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2011 198653 A (TOYOTA MOTOR CORP) 6 October 2011 (2011-10-06) cited in the application paragraphs [0016], [0030], [0051] - [0064] figures 2,3,4	1-18
A	JP 2012 212683 A (HONDA MOTOR CO LTD) 1 November 2012 (2012-11-01) paragraph [0051] table 3	4

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 September 2016	26/09/2016

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Järvi, Tommi

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2016/000893

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2011198653 A	06-10-2011	NONE	
JP 2012212683 A	01-11-2012	JP 5437446 B2	12-03-2014
		JP 2012212683 A	01-11-2012