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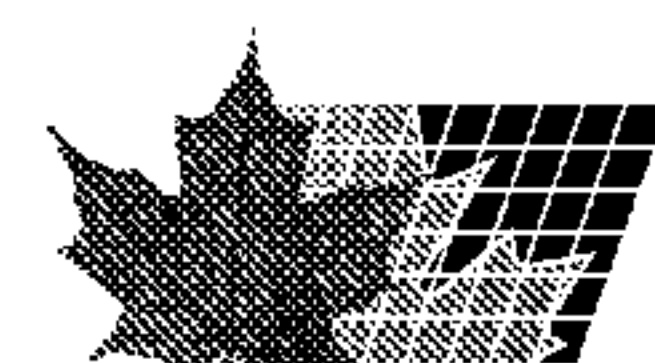
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(54) Titre : PROCEDE POUR FAIRE FONCTIONNER DES PILES A COMBUSTIBLE DIRECTES AU METHANOL

(54) Title: OPERATING CONCEPT FOR DIRECT METHANOL FUEL CELLS

(57) **Abrégé/Abstract:**

The inventive operating concept is provided for effecting the cold start of direct methanol fuel cells. According to the invention, the air is ousted from the cathodes by the residual gas located in the anodes after disconnecting the load (during the preceding operating phase). In addition, cathodic hydrogen is produced by feeding electric energy and is stored. For the start up, air is fed to the cathodes and hydrogen is fed to the anodes during the short-circuit operation. The operation is switched to methanol operation once the operating temperature is reached.



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Abstract

Operating concept for direct methanol fuel cells

The following operating concept is provided for cold-starting direct methanol fuel cells:

- after the load has been disconnected (during the preceding operating phase), the air is removed from the cathodes by the residual anode gas, and hydrogen is evolved at the cathodes by supplying electrical energy and is stored,
- for start-up, in short-circuit operation, air is supplied to the cathodes and hydrogen is supplied to the anodes, and after the operating temperature has been reached operation is switched over to methanol mode.

WO 00/65677

PCT/DE00/01162

Description

Operating concept for direct methanol fuel cells

- 5 The invention relates to a method for operating direct methanol fuel cells, i.e. for operating a stack or a unit comprising fuel cells of this type.

Fuel cells enable energy from a chemical reaction, i.e. chemical energy, to be directly converted into electrical energy. To enable energy converters of this type to find widespread application, it is necessary to solve two significant problems, namely to reduce the costs of producing the units and the peripherals and of providing the fuel. Widespread technical use is expected to come primarily for fuel cells employed in electric traction, i.e. for mobile applications (cf. for example, "Spektrum der Wissenschaft", February 1999, pages A44 to A46).

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The technology of PEM fuel cells (PEM = proton exchange membrane or polymer electrolyte membrane) has proven particularly suitable. This type of fuel cell, which preferably operates at temperatures of between 60 and 80°C, has hitherto been operated with hydrogen H₂ as fuel (cf. for example: "Energie Spektrum", vol. 13, No. 3/98, pages 26 to 29); currently, however, half the rated power, which is based on 60°C, is reached at room temperature. Until the problem of storing H₂ or a widespread network of refueling stations is solved, liquid fuels, such as gasoline and methanol, which are cleaved into hydrogen-rich gas mixtures by means of a reformer, can be used as fuel.

35 In this context, the concept of the direct methanol fuel cell (DMFC) is particularly advantageous. This fuel cell does not require a reformer,

but rather the fuel methanol is converted directly at the anode of a PEM fuel cell (loc. cit., page 28).

However, this results in one difficulty: to achieve current densities of $> 0.1 \text{ A/cm}^2$ which are of interest at a technical level with a cell voltage of not less than 0.5 V, the operating temperature - with the anode catalysts which are currently available - must be $\geq 60^\circ\text{C}$. Therefore, one problem is that of starting a direct methanol fuel cell which has remained in a load-free state for a prolonged period and the temperature of which has therefore fallen to room or ambient temperature. Therefore, experimental tests have proceeded in such a way that the cells are electrically heated externally.

A similar problem arises with PEM fuel cells which are operated with hydrogen and are at a temperature of, for example, approximately -20°C . In this case, the procedure is that at outside temperatures of less than 0°C the cells remain under load. In this way, the heat of reaction which is generated remains in the system and ensures that the internal temperature does not drop below 0°C .

It is an object of the invention to provide a method for operating direct methanol fuel cells which allows the cells to be started even when they have not been operating for a prolonged period or the cell temperature has fallen below the operating temperature (cold start).

According to the invention, this is achieved in the following way:

- after the load has been disconnected, the supply of the gaseous oxidizing agent to the cathodes is interrupted,

WO 00/65677

- 2a -

PCT/DE00/01162

- the oxidizing agent which is present in the cathode chambers is removed by means of the residual anode gas,
- electrical energy is fed to the fuel cells and the
5 hydrogen evolved at the cathodes is stored,
- the supply of energy is interrupted;
for start-up, the cathodes are supplied with gaseous oxidizing agent, and the stored

WO 00/65677

- 3 -

PCT/DE00/01162

hydrogen is fed to the anodes, using short-circuit operation,
- after the operating temperature has been reached, operation is switched to methanol mode and the fuel
5 cells are connected to a load.

The basis for the solution to the problem on which the invention is based is that the direct methanol fuel cell or corresponding unit has been operated for a
10 certain time, i.e. the operating temperature has been reached. If no further power is then required, the cell can be disconnected. Consequently, the temperature within the cell or the unit falls to a temperature of less than 60°C, i.e. to a temperature at which the cell
15 or the unit can no longer be started of its own accord.

Therefore, the invention provides a procedure - after the load has been disconnected - which ensures that the fuel cell or the unit can easily be restarted. This
20 requires a number of steps.

First of all, after the load has been disconnected, the supply of the oxidizing agent, which is preferably air, but may also be oxygen, to the cathodes is interrupted.
25 Then, the gas mixture (residual anode gas) which has formed on the anode side is briefly fed to the cathode chambers, so that the air which is still present in these chambers is flushed out. The residual anode gas which is formed by the anodic oxidation of methanol
30 substantially comprises carbon dioxide and water vapor, as well as (excess) methanol in vapor form.

When the air or oxygen has been removed from the cathode chambers, electrical energy is supplied to the
35 cell or the unit, preferably from a battery or a capacitor. Then, in the process methanol is (continues

WO 00/65677

- 3a -

PCT/DE00/01162

to be) converted at the anodes, but no further oxygen is consumed at the cathodes, but rather hydrogen is generated. This is because the

cathodic load and the absence of oxygen converts the protons which diffuse through the membrane and result from the oxidation of the methanol into gaseous hydrogen, i.e. hydrogen is separated out at the
5 cathodes.

The hydrogen which is formed is stored in a tank. The hydrogen is preferably compressed, for example by means of a restrictor valve, and is then stored under
10 pressure. When the hydrogen tank (gasometer) is full or contains sufficient hydrogen, the supply of current or energy to the unit is switched off. The unit can then cool to room or ambient temperature.

15 When the fuel cell unit is to deliver electrical energy again, the starting operation proceeds in such a way that the cathodes are supplied with oxygen, i.e. air or oxygen is fed to the cathode chambers. However, the anodes are not supplied with methanol, but rather,
20 initially, with the stored hydrogen. For this reason, the unit is immediately able to start and provide electrical energy. This process makes use of the fact that a PEM fuel cell which is supplied with hydrogen is able to function, i.e. begins to operate, even at
25 temperatures of around 0°C. In the process, it heats up, and since initially short-circuit operation is used, as there is as yet no consumer connected, the energy from the hydrogen or the electrical energy which is generated can be completely converted into heat and
30 used to heat up the unit.

After the operating temperature has been reached, preferably after a temperature of $\geq 60^{\circ}\text{C}$ is reached, operation is switched over to methanol mode, i.e. the
35 methanol which is used as fuel is supplied to the anodes in the form of a methanol/water mixture. A load can then be applied to the unit, i.e. the unit can be connected to an (external) consumer.

WO 00/65677

- 5 -

PCT/DE00/01162

In a procedure of this type, it is necessary for the store for the hydrogen required for the starting operation to be dimensioned in such a way that the electrical energy generated during the short-circuit
5 operation is sufficient to bring the fuel cell or the unit up to the temperature required for DMFC operation. However, this is easy to determine by suitable preliminary trials according to the particular application.

WO 00/65677

- 6 -

PCT/DE00/01162

Patent claims

1. A method for operating direct methanol fuel cells, characterized by the following steps:
 - 5 - after the load has been disconnected, the supply of the gaseous oxidizing agent to the cathodes is interrupted,
 - the oxidizing agent which is present in the cathode chambers is removed by means of the residual anode gas,
 - 10 - electrical energy is fed to the fuel cells and the hydrogen evolved at the cathodes is stored,
 - the supply of energy is interrupted;
 - for start-up, the cathodes are supplied with gaseous oxidizing agent, and the stored hydrogen is fed to the anodes, using short-circuit operation,
 - 15 - after the operating temperature has been reached, operation is switched to methanol mode and the fuel cells are connected to a load.
2. The method as claimed in claim 1, characterized in that the gaseous oxidizing agent used is air.
- 25 3. The method as claimed in claim 1 or 2, characterized in that the electrical energy is provided by means of a battery or a capacitor.
4. The method as claimed in one of claims 1 to 3, characterized in that the hydrogen is stored under pressure.
- 30 5. The method as claimed in one or more of claims 1 to 4, characterized in that the changeover to methanol operation takes place at a temperature $\geq 60^{\circ}\text{C}$.
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