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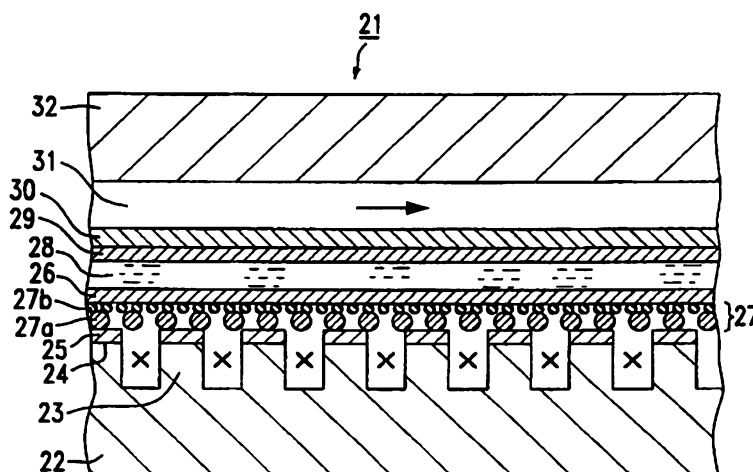
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(54) Title: HIGH-TEMPERATURE FUEL CELL AND STACK OF HIGH-TEMPERATURE FUEL CELLS

(54) Bezeichnung: HOCHTEMPERATUR-BRENNSTOFFZELLE UND HOCHTEMPERATUR-BRENNSTOFFZELLENSTAPEL



(57) Abstract

The present invention relates to a high-temperature fuel cell (11, 21) in which the interconnection circuit plate (12, 22) is located on the anode side of the electrolyte-electrodes unit (17) and is electrically connected to the anode (16, 26). In order to prevent contact problems as the operation duration increases, the anode side of the interconnection circuit plate (12, 22) is further provided with an element for lowering the electric serial resistance of the high-temperature fuel cell (11, 21), such as a layer (25) containing chromium carbide CrxCy.

(57) Zusammenfassung

In einer Hochtemperatur-Brennstoffzelle (11, 21) ist die auf der Anodenseite der Elektrolyt-Elektroden-Einheit (17) liegende Verbundleiterplatte (12, 22) mit der Anode (16, 26) elektrisch verbunden. Um Kontaktschwierigkeiten mit zunehmender Betriebsdauer zu vermeiden, ist erfindungsgemäss auf der Anodenseite der Verbundleiterplatte (12, 22) ein Mittel zum Erniedrigen des elektrischen Serienwiderstands der Hochtemperatur-Brennstoffzelle (11, 21) angeordnet, z.B. eine Chromcarbid CrxCy enthaltende Schicht (25).

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Description

High-temperature fuel cell and stack of high-temperature fuel cells

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The invention relates to a high-temperature fuel cell with at least one interconnector plate and with an electrolyte/electrode unit, and also to a stack of high-temperature fuel cells formed from high-temperature fuel cells of this type.

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It is known that when water is electrolyzed the electrical current breaks down the water molecules into hydrogen (H_2) and oxygen (O_2). A fuel cell reverses this procedure. Electrochemical combination of hydrogen (H_2) and oxygen (O_2) to give water is a very effective generator of electricity. This occurs without any emission of pollutants or carbon dioxide if the fuel gas used is pure hydrogen (H_2). Even with an industrial fuel gas, such as natural gas or coal gas, and with air (which may also have been enriched with oxygen (O_2)) instead of pure oxygen (O_2) a fuel cell produces markedly less pollutants and less carbon dioxide than other energy generators in which the energy is introduced from different sources. The fuel cell principle has been implemented industrially in various ways, and indeed with various types of electrolyte and with operating temperatures of from 80°C to 1000°C .

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Depending on their operating temperature, fuel cells are divided into low-, medium- and high-temperature fuel cells, and these in turn have a variety of technical designs.

In the case of a stack of high-temperature fuel cells composed of a large number of high-temperature

fuel cells, there is an upper interconnector plate which covers the stack of high-temperature fuel cells, and under this plate there are, in this order, at least one protective layer, one contact layer, one
5 electrolyte/electrode unit, one further contact layer, one further interconnector plate, etc.

The electrolyte/electrode unit here comprises two electrodes - one anode and one cathode - and a solid
10 electrolyte designed as a membrane arranged between anode and cathode. Each electrolyte/electrode unit here situated between two adjacent interconnector plates forms, with the contact layers situated immediately adjacent to the electrolyte/electrode unit on both
15 sides, a high-temperature fuel cell, which also includes those sides of each of the two interconnector plates situated on the contact layers. This type of fuel cell, and other types, are known from the "Fuel Cell Handbook" by A. J. Appleby and F. R. Foulkes,
20 1989, pp. 440-454, for example.

A single high-temperature fuel cell provides an operating voltage of less than one volt. A stack of high-temperature fuel cells is composed of a large
25 number of high-temperature fuel cells. The connection in series of a large number of adjacent high-temperature fuel cells can give an operating voltage of some hundreds of volts from a fuel-cell system. Since the current provided by a high-temperature fuel cell is
30 high - up to 1000 amperes in the case of large high-temperature fuel cells - the electrical connection between the individual cells should preferably be one which gives rise to particularly low series electrical resistance under the abovementioned conditions.

The electrical connection between two high-temperature fuel cells is provided by an interconnector plate, via which the anode of one high-temperature fuel cell is connected to the cathode of the next high-temperature fuel cell. The interconnector plate therefore has an electrical connection to the anode of a high-temperature fuel cell and to the cathode of the next high-temperature fuel cells. The electrical connection between the anode and the interconnector plate is provided by an electrical conductor which may take the form of a nickel grid (see, for example, DE 196 49 457 C1). It has been found here that the series electrical resistance between nickel grid and interconnector plate is high, at some hundreds of mOhm cm². This has a severe adverse effect on the electrical performance of the stack of high-temperature fuel cells.

It is an object of the invention to improve a high-temperature fuel cell of the type mentioned at the outset so as to avoid any relatively high series electrical resistance and to ensure high conductivity, even over prolonged periods. A further object of the invention is to improve a stack of the type mentioned at the outset of high-temperature fuel cells so as to avoid any relatively high series electrical resistance and to ensure high conductivity, even over prolonged periods.

The first object mentioned is achieved by way of a high-temperature fuel cell of the type mentioned at the outset in which, according to the invention, a means for lowering the series electrical resistance of the high-temperature fuel cell has been arranged on that side of the interconnector plate which faces toward the anode of the electrolyte/electrode unit.

Experiments with a stack of high-temperature fuel cells and appropriate modeling experiments have shown that, even after a short period of operation, an oxide layer

forms between a nickel grid and an interconnector plate composed of $\text{CrFe}_5\text{Y}_3\text{O}_3$. An oxide layer develops here on the surface of the side of the interconnector plate which faces toward the space through which the fuel gas passes in the high-temperature fuel cell, which layer is probably composed of a CrNi spinel where the nickel grid and interconnector plate are in cohesive contact, and of Cr_2O_3 where they are in non-cohesive contact.

If, for example, an electron-beam welding process has been used to give the nickel grid nine points of contact with the interconnector plate, these welded contact points then form only a fraction ($<0.1\%$) of the total number of contact points which connect the nickel grid electrically to the interconnector plate. The majority of the contact points are pressure contacts arising where the nickel grid presses onto the interconnector plate. These pressure contacts are situated on the oxide layer which forms during operation of the high-temperature fuel cell and as operation continues grows into the interconnector plate in compliance with a parabolic function.

There is therefore a poorly conducting oxide layer between the nickel grid and the interconnector plate, and this has an adverse effect on the series resistance of high-temperature fuel cells connected in series. The chromium oxide forms even when the partial pressure of oxygen is about 10^{-18} bar. These partial pressures of oxygen are always present during normal operation of the high-temperature fuel cell.

The invention is based on the idea that suppressing the formation of the oxide layer on the interconnector plate avoids any relatively high series electrical resistance and ensures high conductivity even over prolonged periods. This is reliably achieved during the

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operation of the high-temperature fuel cell by the
arrangement on the interconnector plate of a means of

preventing oxidation of the interconnector plate. Such a means of preventing oxidation of the interconnector plate is therefore a means of lowering the series electrical resistance during the operation of the high-
5 temperature fuel cell below that of a cell which does not comprise this means.

It is advantageous for a means of this type to be applied in the form of a protective layer of chromium
10 carbide Cr_xC_y onto the fuel-gas side of the interconnector plate. A protective layer of this type does not oxidize under operating conditions; it is therefore oxidation-resistant. A layer of this type should be gas-tight when applied, so as to be
15 impermeable to oxygen. Comprehensive experimentation has shown that oxidation of the interconnector plate is reliably prevented to a very large extent by a layer of chromium carbide Cr_xC_y . It is also cost-effective and easy to handle.

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It is advantageous to use chromium carbide Cr_3C_2 , CrC , Cr_7C_3 , or Cr_{23}C_6 . A layer which comprises one or more of these compounds is highly electrically conducting. This means that the layer causes no, or only insignificant,
25 impairment of the electrical connection between anode and interconnector plate. A layer of this type is usually very resistant to corrosion at the partial pressures of oxygen usually prevailing on the fuel-gas side of the interconnector plate during operation of
30 the high-temperature fuel cell. It is moreover chemically resistant to the operating media which pass over the fuel-gas side of the interconnector plate during operation - for example methane or gases derived from carbon.

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An appropriate thickness for the layer is from 5 μm to 10 μm . A chromium carbide layer of this thickness is

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particularly effective in preventing oxidation of the fuel-gas side of the interconnector plate.

In another advantageous embodiment of the invention, a nickel grid has been arranged between the interconnector plate and the anode of the electrolyte/electrode unit and has been connected
5 electrically to the interconnector plate. The nickel grid may also be a nickel grid package which comprises a relatively thin contact grid and a relatively thick carrier grid. The material nickel is particularly advantageous, since it does not oxidize at the partial
10 pressures of oxygen usually prevailing on the fuel-gas side during operation of the high-temperature fuel cell. Nickel is moreover cost-effective and easy to handle. A grid manufactured from nickel is flexible and, even if simply situated on the interconnector
15 plate, ensures sufficient electrical contact between interconnector plate and nickel grid. This contact is retained even during temperature variations within the high-temperature fuel cell.

20 A thin chromium carbide layer is electrically conductive, and the initial conductivity of the composite of interconnector plate plate/chromium carbide layer/nickel grid is therefore practically retained for the entire period of operation. This
25 electrical conductivity of the chromium carbide layer means that even the mechanical contact produced by lying against the chromium carbide layer connects the nickel grid to the interconnector plate plate. A better electrical and mechanical connection between nickel
30 grid and connector plate plate is achieved by welding the nickel grid onto the interconnector plate plate. Spot welding is an appropriate process for this. In cases where the nickel grid has been point-attached to the interconnector plate plate the spot welds extend
35 through the chromium carbide layer and connect the nickel grid to the interconnector plate plate.

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Cost-effective processes can be used to coat the interconnector plate plate with a thin chromium carbide layer. The coating may take place by a

PVD (physical vapor deposition) process, for example. A process of this type is sputtering - for example in pure argon, electron-beam vapor deposition or laser-beam vapor deposition. These processes can be used to
5 coat one side of the interconnector plate. The coating temperature is below 500°C.

An alternative to the PVD process is a CVD process (chemical vapor deposition). In this thermal coating
10 process the substance to be coated is produced in the gas phase by the chemical decomposition of starting materials and applied to the component to be coated.

In another advantageous embodiment of the invention,
15 the interconnector plate consists of $\text{CrFe}_5\text{Y}_2\text{O}_3$, i.e. of 94% by weight of chromium, 5% by weight of Fe and 1% by weight of Y_2O_3 . An interconnector plate of this type has proven in numerous experiments to be suitable for operation in an high-temperature fuel cell. It can also
20 easily be coated with a chromium carbide layer.

The second object mentioned is achieved by means of a stack of the type mentioned at the outset of high-temperature fuel cells which comprises high-temperature
25 fuel cells in which according to the invention a means for lowering the series electrical resistance of the high-temperature fuel cell has been arranged on that side of the interconnector plate which faces toward the anode of the electrolyte/electrode unit.

30 To avoid repetition, for the description of other embodiments and advantages of the invention reference is made to the statements made above.

35 Examples of the invention are described in more detail below using two figures, in which

FIG. 1 shows a diagram of a section of a high-temperature fuel cell;

FIG. 2 shows a detailed diagram of a section of a high-temperature fuel cell;

Fig. 1 shows a diagram of a section of an interconnector plate 12 of a high-temperature fuel cell 11. The surface 14 of the fuel-gas side of the interconnector plate 12 - i.e. that surface which faces toward the anode 16 of the electrolyte/electrode unit 17 of the high-temperature fuel cell 11 - has been coated with a layer 15 of chromium carbide Cr_2C_3 . The interconnector plate 12 has been electrically connected to the anode 16 by an electrical conductor not shown in the figure. The intervening space between the anode 16 and the layer 15 is a section of the fuel gas space of the high-temperature fuel cell 11. The layer 15 effectively and reliably prevents oxidation of the fuel-gas side of the interconnector plate 12 during operation of the high-temperature fuel cell 11.

Figure 2 shows a detailed diagram of a section of a high-temperature fuel cell 21. An interconnector plate 22 of $\text{CrFe}_5\text{Y}_2\text{O}_3$ has been provided with a number of protuberances 23, between which have been formed channels running perpendicularly to the plane of the paper for operating media. These channels are supplied with a fuel gas, such as hydrogen, natural gas or methane. The surface 24 of the interconnector plate 22 has been provided with a thin layer 25 of chromium carbide CrC , of about $10\text{ }\mu\text{m}$ thickness. The layer 25 has been applied by a PVD process. The nickel grid 27 has been connected electrically and mechanically to the interconnector plate 22 by spot welds which extend through the layer 25 of chromium carbide. For clarity

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the spot welds are not shown in the figure. The nickel grid 27 here is a nickel grid package consisting of a

- coarse, relatively thick nickel carrier grid 27a and of a fine, relatively thin nickel contact grid 27b. Adjacent to the nickel grid 27 is is a thin anode 26, on the far side of which is a solid electrolyte 28.
- 5 This solid electrolyte 28 has a cathode 29 on its upper side. The cathode 29 is adjoined by a contact layer 30 and another interconnector plate 32, only the lower part of which is shown. A number of channels 31 for operating media have been made in the interconnector
- 10 plate 32, but only one of these is shown. The channels 31 for operating media run parallel to the plane of the paper, and oxygen or air passes through these during operation of the high-temperature fuel cell 21.
- 15 The unit consisting of cathode 29, solid electrolyte 28 and anode 26 is termed the electrolyte/electrode unit.

The layer 25 of chromium carbide shown in Figure 2 prevents damaging oxidation of the interconnector

20 plate 22 lying beneath the same during operation of the high-temperature fuel cell 21. In particular, corrosion below the surface of the spot welds is also suppressed. This gives the high-temperature fuel cell 21 low series resistance which increases only insignificantly, or not

25 at all, as the period of operation continues.

A number of these high-temperature fuel cells 21 may be brought together to give a stack of fuel cells or "stack".

Patent claims

1. A high-temperature fuel cell (11,21), with at least one interconnector plate (12,22) and with an electrolyte/electrode unit (17), characterized in that a means for lowering the series electrical resistance of the high-temperature fuel cell (11,21) has been arranged on that side of the interconnector plate (12,22) which faces toward the anode (16,26) of the electrolyte/electrode unit (17).
2. A high-temperature fuel cell (11,21) as claimed in claim 1, characterized in that the means provided comprises a layer (15,25) comprising chromium carbide Cr_xC_y .
3. A high-temperature fuel cell (11,21) as claimed in claim 2, characterized in that the chromium carbide used comprises Cr_3C_2 , CrC , Cr_7C_3 , or Cr_{23}C_6 .
4. A high-temperature fuel cell (11,21) as claimed in claim 2 or 3, characterized in that the layer (15,25) has a thickness of from 5 μm to 10 μm .
5. A high-temperature fuel cell (11,21) as claimed in any of claims 1 to 4, characterized in that a nickel grid (27) has been arranged between the interconnector plate (12,22) and the anode (16,26) of the electrolyte/electrode unit (17) and has been connected electrically to the interconnector plate (12,22).
6. A high-temperature fuel cell (11,21) as claimed in any of claims 1 to 5, characterized in that the nickel grid (27) has been fused onto the interconnector plate (12,22) by the layer (15,25), preferably by means of a spot welding process.

7. A high-temperature fuel cell (11,21) as claimed in any of claims 1 to 6, characterized in that the layer has been applied to the interconnector plate (12,22) by means of PVD processes or CVD processes.

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8. A high-temperature fuel cell (11,21) as claimed in any of claims 1 to 7, characterized in that the interconnector plate (12,22) is composed of $\text{CrFe}_5\text{Y}_2\text{O}_3$.

10 9. A stack of high-temperature fuel cells which has a large number of interconnector plates (12,22,32) arranged one on top of the other with an electrolyte/electrode unit (17) situated between each two interconnector plates (12,22,32), where each two
15 adjacent interconnector plates (12,22,32) form a high-temperature fuel cell (11,21) as claimed in any of claims 1 to 8.

Abstract

High-temperature fuel cell

5 In a high-temperature fuel cell (11,21), the
interconnector plate (12,22) situated on the anode side
of the electrolyte/electrode unit (17) has been
electrically connected to the anode (16,26). To prevent
contact problems as the duration of operation
10 increases, the invention arranges, on the anode side of
the interconnector plate (12,22), a means of lowering
the series electrical resistance of the high-
temperature fuel cell (11,21).

15 FIG 2

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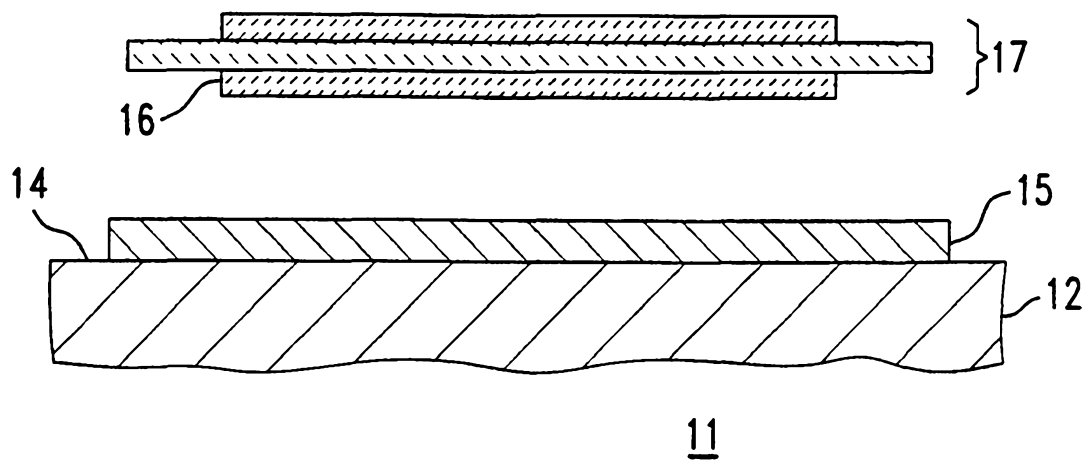


FIG 1

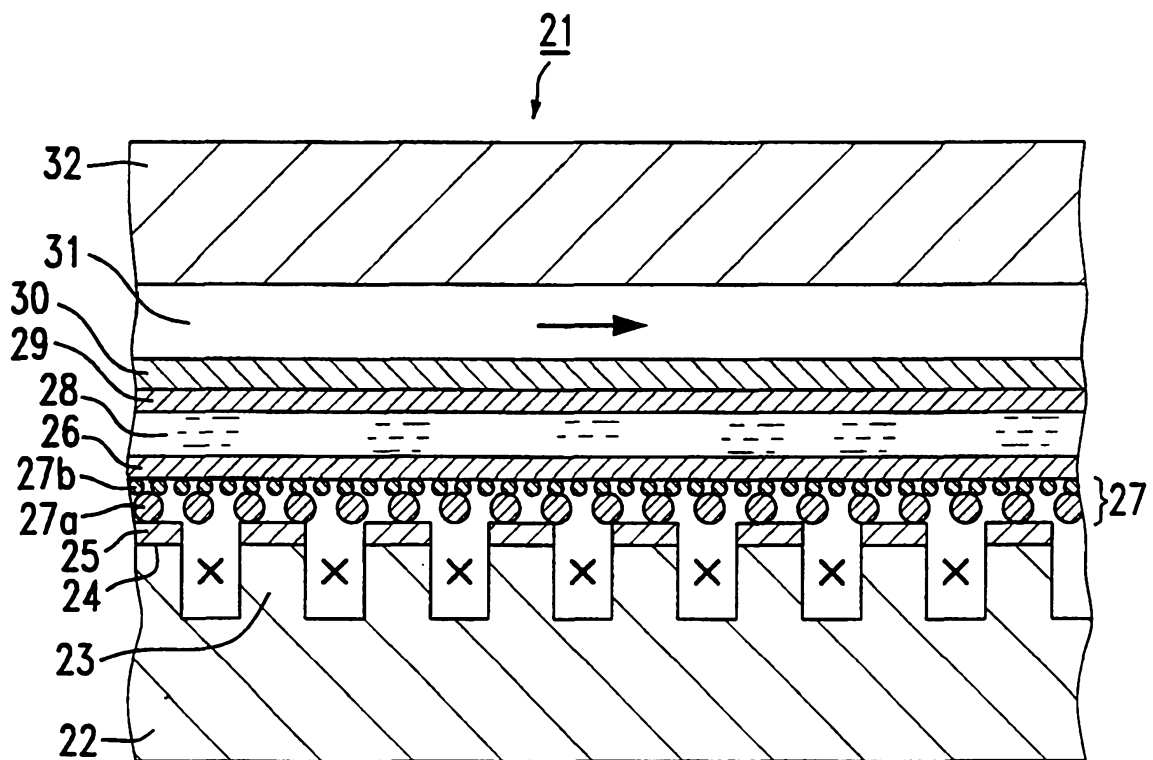


FIG 2