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(54) Title: ANODE ASSEMBLY FOR AN ELECTROCHEMICAL CELL

(57) Abstract: Anode assembly consisting of an anode cermet (2) and an auxiliary layer (3) positioned between the anode cermet and the electrolyte (1). According to the invention this anode cermet comprises a mixture of metals and metal oxides and oxygen ion-conducting oxide. In order to improve the adhesion of this layer to the electrolyte under mechanical stress, which arises in particular in the case of a change in temperature and gas disruptions as a consequence of system malfunctions, it is proposed to produce the auxiliary layer from a material that essentially comprises oxygen ion-conducting oxide. In order to improve the contact with the current collector it is proposed to apply a contact layer (4) essentially consisting of metal (oxide) particles between the anode cermet (2) and the current collector (5).

ANODE ASSEMBLY FOR AN ELECTROCHEMICAL CELL

The present invention relates to an anode assembly for an electrochemical cell, comprising an anode cermet and an auxiliary layer applied thereon on the electrolyte side, said anode comprising a semi-noble metal oxide and an oxide that conducts oxygen ions.

Such an assembly with an auxiliary layer is disclosed in Japanese Patent Application 9/190824. With this known assembly the auxiliary layer adjacent to the electrolyte contains 5 % nickel oxide. In European Patent Application 0 672 306 the anode cermet consists of YSZ (yttrium-stabilised zirconia) and a metal (oxide). In order to improve the yield of the cell it is proposed to apply an auxiliary layer between the anode cermet and the electrolyte.

By this means the oxygen ion conduction and electron conduction are optimised. This is achieved mainly as a result of the characteristic that the auxiliary layer consists of metal particles for electron conduction and electrocatalytic activity and oxides for promoting oxygen ion conduction and mechanical stability.

Nowadays doped ceria is used instead of yttrium-stabilised zirconia as the base material for the cermet, in which, of course, metal (oxide) is present. When operating fuel cells in practice it has been found that conditions can arise which cannot be regarded as normal but which it is virtually impossible to avoid in practice. For instance, it is possible that under extreme operating conditions the anode is exposed to oxidising gases. The metal particles in the anode, which in general are applied in the oxide form in the anode but which reduce to metal particles on sintering or starting up, will reoxidise as a result. This results in a change in volume of the layer concerned, caused by the change in volume from metal particles to metal oxide particles.

Operating conditions of this type arise when a fuel cell is in standby mode. Under these conditions the reducing gas is not present and, as a result of oxidation of the metal particles, which in general comprise a semi-noble metal such as nickel, copper or silver and more particularly nickel, the volume increases as a result of the formation of, for example, nickel oxide. Theoretically such a standby mode will not arise, but it nevertheless occurs with some regularity in practice in the event of malfunction.

Appreciable stresses arise as a result of the increase in volume. Consequently it can arise that the anode cermet makes inadequate contact with the electrolyte, as a result of which a dramatic reduction in the yield of the fuel cell occurs.

The aim of the present invention is to improve the mechanical adhesion of the anode

layer/electrolyte layer under such conditions, that is to say even in the situation in which oxidation, that is to say an increase in the volume of the anode cermet, takes place it must always be ensured that there is still adequate contact between the anode and the electrolyte during the subsequent operation, where the oxides are reduced again.

5 This aim is achieved with an anode assembly as described above in that said auxiliary layer contains approximately 100 % oxygen ion-conducting oxides.

It has been found that a strong mechanical joint between the electrolyte layer and the anode layer is obtained by the use of an auxiliary layer that essentially consists completely of oxygen ion-conducting oxide. By not applying any nickel oxide or other metal oxide in
10 the auxiliary layer, it can be guaranteed that an essentially defect-free auxiliary layer is produced. As a result the strength of the auxiliary layer can be optimised and there is no longer a risk of the anode assembly detaching from the electrolyte during heating or sintering.

A defect-free auxiliary layer can be obtained by adding sinter-active substances to the
15 auxiliary layer in a concentration of up to 5 % (mol/mol). Moreover, the auxiliary layer is sinter-active towards the adjacent layers as a result. After sintering the auxiliary layer, the sinter-active substance present therein will be taken up in the crystal lattice of the oxygen-ion conducting oxide, as a result of which the mechanical properties of the auxiliary layer do not change substantially and the auxiliary layer still consists essentially completely of
20 oxygen ion-conducting oxide.

Examples of sinter-active substances are Co, Ni and Mn. Usually these substances will oxidise easily, but because they are incorporated into the oxygen ion-conducting oxide of the auxiliary layer such oxidation no longer takes place.

The actual anode can be made up in the conventional manner, as is known from the
25 prior art, provided the condition that the oxide particles in the cermet are sinter-active is met, as a result of which a good adhesion with the oxide particles in the auxiliary layer is obtained.

Ceria doped with gadolinium has been mentioned above as an example of the oxygen ion-conducting oxide. More particularly, the oxygen ion-conducting oxides according to
30 the invention are fluorite oxides, such as CeO_2 , ZrO_2 , ThO_2 , Bi_2O_3 , HfO_2 on their own or doped with alkali metal oxides (for example MgO , CaO , SrO , BaO) or rare earth oxides (for example Gd_2O_3 , Sm_2O_3 , Y_2O_3). In this context fluorite oxides which display a high degree of electrical conduction and mechanical, chemical and thermal stability are

preferred.

The auxiliary layer described above preferably has a thickness of between 0.1 and 10 μm . Ion conduction is guaranteed by the presence of the doped cerium oxide. This oxide must also be chemically compatible with the oxide present in the anode cermet. Therefore
5 the same cerium oxide is preferably used both for the anode cermet and for the auxiliary layer.

As a result of the presence of an auxiliary layer having a high cerium oxide concentration, the effect of depletion of the cerium oxide from the anode to the electrolyte by diffusion processes at elevated temperature, such as arises during sintering and/or
10 operation of the cell, will be avoided. Consequently, the yield of the anode can be ensured for a prolonged period.

The actual anode can be made up in a conventional manner. According to a preferred embodiment of the invention, the thickness of the anode is between 5 and 100 μm . In contrast to previous proposals, it is desirable that, in view of the mechanical stress to which
15 such an anode cermet is subjected on start-up, cooling and reduction/oxidation, the mechanical strength is appreciable. That is to say it is desirable that the cerium oxide particles form a structure which does not essentially deform on the one hand under high fuel utilisation and on the other hand when a fuel gas is not present. Moreover, it is important that the metal (nickel) particles do not sinter together during operation because
20 this causes the strength of the anode microstructure and the electrocatalytic activity of the metal particles to decrease. The aim is for a fine microstructure with a particle size of less than 1 μm . As a result of the use of this relatively small particle size, the metal particles are not able or are barely able to post-sinter during operation after the actual sintering process.

Apart from the particle size, the porosity must also be maintained. This is preferably
25 in the range between 10 and 50 % (V/V).

In order to improve the contact between the anode and the current collector and, moreover, to counteract the effect of nickel evaporating out of the actual anode, it is proposed according to the invention to apply a contact layer that is essentially metallic, that is to say essentially consists of nickel when nickel is used in the anode. Such a layer is also
30 found to have ductile characteristics, as a result of which the effect of the increase in volume caused by oxidation can be absorbed. Such a metallic anode contact layer preferably has a thickness of between 3 and 10 μm . Differences in thermal expansion between the anode and the current collector are absorbed with such a layer.

Although it is simple to allow such a contact layer to extend over the entire anode/current collector interface, in principle the presence of this layer is necessary only at those locations where current is taken off.

The application of the anode and, respectively, the anode auxiliary layer can take place using any method known in the state of the art, such as tape casting. According to an advantageous embodiment of the invention, the screen printing technique is used for this purpose. After all, by this means it is possible to obtain the small layer thickness described above. With this procedure the starting material used is preferably a sintered electrolyte based on stabilised zirconia (YSZ). This preferably has a thickness of between 50 and 200 μm . With this procedure, in contrast to the prior of the art, an anode intermediate layer is first applied. In the state as applied, this contains at least 95 % (m/m) cerium oxide doped with gadolinium. After drying at a relatively low temperature (such as 75 °C), this assembly is heated in a furnace at a temperature of at most 950 °C. As a result, the organic material (binder) in the layer applied by screen printing is driven off. The anode intermediate layer is not compacted by this relatively low temperature.

After cooling, the anode cermet is applied to the free side of the anode auxiliary layer. The anode cermet consists of a mixture of, for example, 65 % (m/m) metal oxide and 35 % (m/m) doped cerium oxide. This application can also take place by means of screen printing. Before sintering the various components, a contact layer consisting of a pure metal oxide in which the metal concerned is the same as the metal that is present in the anode cermet is first applied to the free side of the cermet.

A second sintering treatment then follows, in which the microstructure is compacted and rigidity is obtained. Finally, the cathode is then applied on the other side of the electrolyte and the whole is sintered again. The metal oxide described above on the anode side can be reduced to a metal during this final sintering step and will be reduced to a metal when starting up, as a result of the presence of reducing gases.

The invention will be explained in more detail below with reference to an illustrative embodiment shown in the drawing.

In the drawing:

Fig. 1 shows, diagrammatically in cross-section, part of an electrochemical cell according to the invention; and

Fig. 2 shows a graph which shows the long-term performance of a cell according to the invention.

An electrolyte consisting of a sintered electrolyte, for example based on stabilised zirconia, is indicated by 1. An anode 6 is applied to this in the manner described above. This anode consists of an anode adhesion layer 3 which forms the join between the electrolyte 1 and the anode cermet 2. This anode adhesion layer promotes the adhesion of the anode cermet to the electrolyte. The anode adhesion layer essentially consists of doped cerium oxide. As a result of the essential absence of metals, should oxidation of metal particles take place, as a result of which an increase in volume in the anode cermet occurs, such a change in volume will not take place in the anode adhesion layer. However, as a result of the presence of the same cerium oxide there is good adhesion between layer 2 and layer 3, which is well able to resist an increase in volume as a result of oxidation of metal particles. On the other hand, the anode adhesion layer adheres particularly well to electrolyte 1.

An anode contact layer 4 which preferably consists of pure metal particles is applied to the anode cermet 2. The current collector is indicated by 5. It must be understood that the anode adhesion layer does not have to extend over the entire surface of the anode cermet 2 but can be applied locally only, in the locations where current take-off by current collector 5 takes place.

The invention will be explained in more detail below with reference to an example.

Example

The starting material used is a sintered electrolyte comprising yttrium-stabilised zirconia with a thickness of 140 μm .

An intermediate layer with a thickness of 10 μm is applied to this with the aid of a screen printing technique. This intermediate layer is based on cerium oxide doped with gadolinium. In addition, a sinter-active component such as 2 % (mol/mol) cobalt is added to this layer. This assembly is heated at a temperature of 75 °C for two hours in a conventional drying oven. Sintering is then carried out for one hour at 600 °C to drive off the binder.

After cooling, an anode cermet consisting of a mixture of 65 % (m/m) nickel oxide and 35 % (m/m) cerium oxide doped with gadolinium is screen printed. This layer has a thickness of approximately 50 μm . Immediately thereafter a layer with a thickness of 20 μm consisting of pure nickel oxide is screen printed thereon. The various layers are then

sintered at a temperature of 1400 °C for one hour.

After cooling, a cathode layer consisting of lanthanum manganite doped with strontium and yttrium-stabilised zirconia is applied to the other side of the electrolyte. The whole is then sintered at 1200 °C.

- 5 Experiments have shown that a cell that has been produced in the abovementioned manner gives a stable performance for 800 hours, including three oxidation/reduction cycles on the anode side. See Fig. 2 (endurance test graph). In this figure hydrogen (1.9 g/h) was used as fuel and air (155 g/h) as oxidising agent in an endurance test. The effective surface area was 100 cm² in a ceramic housing with Pt current collector for the
- 10 cathode and an Ni current collector for the anode.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Method for producing an anode electrolyte assembly (6) for an electrochemical cell, comprising an anode cermet (2), an electrolyte and an auxiliary layer (3) applied between said cermet (2) and said electrolyte (1) side, said anode comprising a semi-noble metal oxide, such as a nickel, copper and silver oxide, and an oxide that conducts oxygen ions, wherein said auxiliary layer contains oxygen ion-conducting oxides, said assembly being electrolyte supported and said auxiliary layer consisting essentially completely of oxygen ion-conducting oxides, wherein said auxiliary layer is provided by screen printing or tape casting and has a thickness of between 0.1 and 10 μm .
5
2. Method according to claim 1, wherein said anode cermet contains Ni.
3. Method according to one of the preceding claims, containing a contact layer containing metal particles applied on the other side of the anode.
- 15 4. Method according to claim 3, wherein the metal particles in the anode cermet match the metal particles in the contact layer.
5. Method according to claim 3 or 4, wherein said contact layer has a thickness of between 3 and 10 μm .
- 20 6. Method according to one of the preceding claims, wherein said oxygen ion-conducting oxide comprises an oxide of fluorite type structure.
7. Method according to claim 6, wherein said fluorite oxide has been doped with oxides of alkali metals or oxides of rare earths.

8. Method according to one of the preceding claims, wherein said anode
cermet comprises an oxygen ion-conducting oxide and wherein said
auxiliary layer is chemically compatible with said oxygen ion-conducting
oxide.

5

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Fig 1

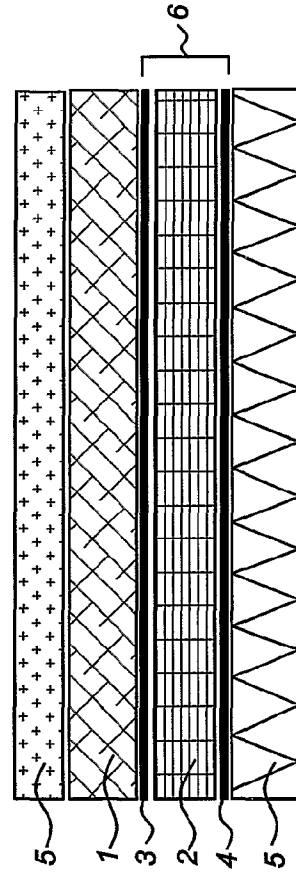


Fig 2