NASA CASE NO. NPO-10537-1

PRINT FIG. The Figure

N72-10138

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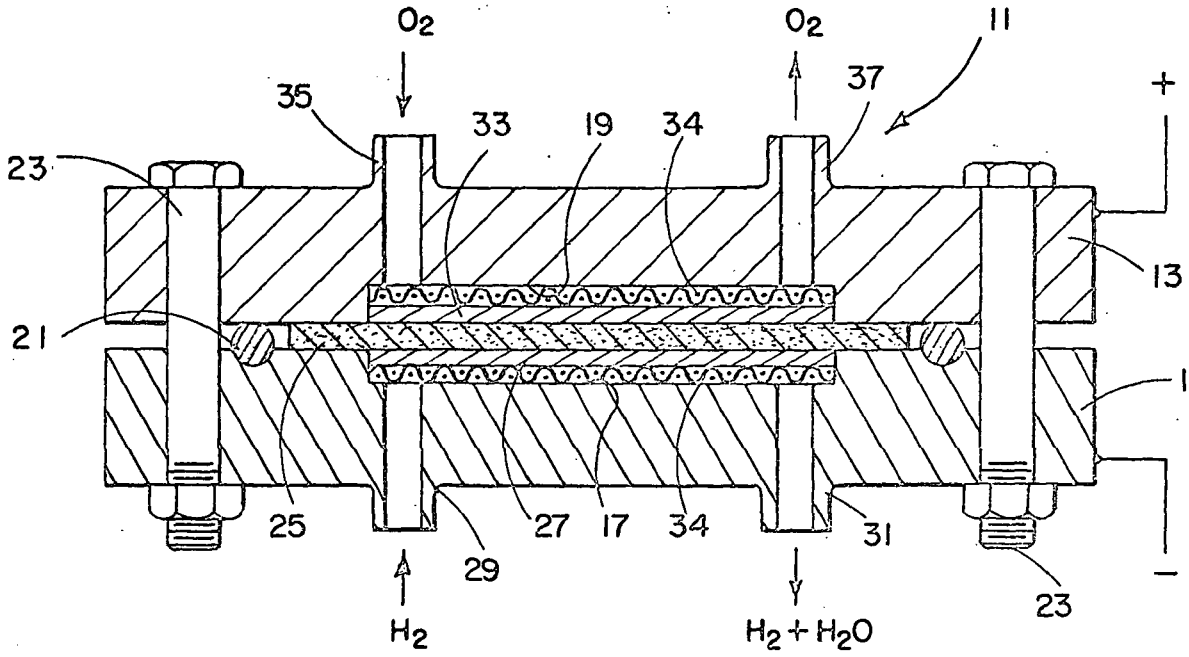

INVENTOR

LARRY L. SWETTE

BY

ATTORNEYS

(3)

Inventor: Larry Leroy Swette NASA Case HQN-10537-1
Contract NASw-1233
Contractor: Tyco Laboratories, Inc. December, 1970

ELECTROCATALYST FOR OXYGEN REDUCTION

The object of this invention is to provide a new catalyst composition useful for electrochemical oxygen reduction in low temperature alkaline fuel cells. Further, an object of the invention is to provide a catalyst which has improved properties over those previously utilized, as well as being less expensive.

The figure discloses a typical alkaline fuel cell for the electrochemical oxygen reduction. As seen in the figure, the fuel cell 11 contains cell plates 13 and 15 which have cavities 17 and 19 formed at the centers thereof. An O-ring seal 21 surrounds the cavities. Disposed between the plates is an electrolyte 25 containing an aqueous solution of potassium hydroxide in a suitable matrix. On one side of the electrolyte is a hydrogen oxidation anode 27 of conventional construction such as platinum black dispersed in a binder therefor. The anode 27 is maintained in place by screens 34. Hydrogen is directed through an inlet 29 and exits through line 31. Disposed on the opposite side of the electrolyte is the oxygen reduction electrode 33 of this invention which is comprised of a mixture of platinum and silver dispersed in a suitable inert binder such as tetrafluoroethylene. The catalytic mixture will contain from 20 to 40 atomic percent platinum with the remainder being silver. An inlet 35 directs oxygen gas to cavity 19 while exit line 37 will conduct excess oxygen. The reaction of the above described fuel cell involves in the anode

$$H_2 + 2OH \rightarrow 2H_2O + 2e^-.$$

At the cathode of the cell, the reaction is

$$1/2\ O_2 + H_2O + 2e^- \rightarrow 2OH.$$

A preferred composition for the catalyst of this invention is 30 atomic percent platinum with the remainder silver. Thus a typical electrode having a loading of 20 mg/cm^2 of catalyst, would have a platinum loading of 8.6. Such an electrode will provide better performance than a similar one having a platinum loading of 20 mg/cm^2 and performance equivalent to available electrodes having a platinum loading of 40 mg/cm^2. Thus it can be seen that the herein catalyst will contain significantly less platinum than previous electrodes while providing superior results.

Contractor: TYCO Laboratories, Inc.
Bear Hill
Waltham, Mass. 02154

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TYCO Laboratories, Inc.
Contract NASw-1233

S P E C I F I C A T I O N

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN THAT, Larry Leroy Swette, a citizen of the United States of America, residing at Belmont, in the County of Middlesex, State of Massachusetts, has invented a new and useful

ELECTROCATALYST FOR OXYGEN REDUCTION

of which the following is a specification.

ABSTRACT OF THE DISCLOSURE

A catalyst composition useful for electrochemical oxygen reduction in low temperature alkaline fuel cells comprised of platinum and silver which are dispersed in a resinous inert binder to provide a cell electrode.

ORIGIN OF THE INVENTION

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 Stat. 435; 42 USC 2457).

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention is in the field of fuel cells. More particularly the invention relates to an electrode composition useful in oxygen reduction in low temperature alkaline fuel cells.

2. Description of the Prior Art

Pure platinum catalysts have been considered as the best catalysts for electrochemical oxygen reduction in low temperature alkaline fuel cells. However, pure platinum catalysts are expensive due to the high cost of the material. Further,

the pure platinum catalysts have exhibited structural problems indicated by drastic voltage loss at some limiting or high current density.

Thus it is an object of this invention to provide an improved catalyst for electrochemical oxygen reduction as compared to a pure platinum catalyst.

Another object of this invention is to provide a less expensive catalyst than a pure platinum catalyst for electrochemical oxygen reduction.

SUMMARY OF THE INVENTION

The above and other objects of the invention are accomplished by a novel catalyst composition which is comprised of 20 to 40 atomic percent platinum with the remainder being silver. The platinum and silver is in powder form and mixed with a suitable binder, polytetrafluoroethylene. The resulting electrode is formed by pressing the material together, drying it, and then heating it to a point sufficient to sinter the binder. The formed electrode is at least as active as one containing only platinum and is structurally superior to platinum for high current density operation. It is believed the invention will be further understood from the following detailed description and drawings in which

BRIEF DESCRIPTION OF THE DRAWINGS

The figure represents a cross sectional view of an alkaline fuel cell incorporating the catalyst of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Turning to the figure, there is an illustration of a type of fuel cell in which the catalyst electrodes of this

invention are typically utilized. The fuel cell 11 is comprised of cell plates 13 and 15. The plates have cavities 17 and 19 respectively formed at the center thereof and facing each other. The o-ring seal 21 circumferentially surrounds the cavities 17 and 19 and is held in place by bolts 23 that secure the two cell plates 13 and 15 together. Disposed between the two plates is an electrolyte 25. The electrolyte can be of a conventional material such as a 35 weight percent KOH in an aqueous solution in an asbestos matrix. The cell will typically contain a hydrogen oxidation electrode 27 which once again can be of a conventional construction such as a tetrafluoroethylene bonded platinum black material having a loading of 40 mg/cm^2 of platinum on a nickel screen. The electrode 27 is disposed adjacent the electrolyte matrix 25 and held in place by screens 34 or expanded metal structures. This leaves the gas cavity 17 to which an inlet 29 and separate outlet 31 are connected. Hydrogen is directed through the inlet 29 and exits through line 31. This results in plate 15 being the anode or negative plate of the cell as will be further explained. Disposed on the opposite side of the electrolyte 25 from the hydrogen anode is the oxygen reduction electrode 33 of this invention. The electrode 33 will be comprised as will be further described with a mixture of platinum and silver on a suitable screen utilizing an inert binder such as tetrafluoroethylene.

An inlet 35 directs oxygen gas to the cavity 19 adjacent the oxygen reduction catalytic surface 33. An exit line 37 from the cavity 19 will conduct excess oxygen from the fuel cells on the oxygen cathode side thereof. This results in plate 13 becoming

the cathode or positive plate of the fuel cell. The reaction in the above described fuel cell involved at the anode is

$$H_2 + 2\ OH^- \rightarrow 2H_2O + 2\ e^-.$$

In the cathode of the cell, the reaction is:

$$1/2O_2 + H_2O + 2\ e^- \rightarrow 2OH^-.$$

The overall reaction in the fuel cell is:

$$H_2 + 1/2O_2 \rightarrow H_2O.$$

As indicated, the herein invention is particularly directed to the oxygen reduction catalyst to be used in the electrode 33 of the alkaline fuel cell. Previous to the herein invention, pure platinum catalysts were utilized. Such a pure platinum catalyst was comprised of pressing platinum powder on a suitable screen such as a nickel screen and bonding the powder with an inert resin such as tetrafluoroethylene or the like. The typical loading of the platinum was in the range of 10 mg/cm^2 to 40 mg/cm^2. It is believed that a particular structure is required for optimum mass transfer of reactants and products to and from catalytic sites on electrode structures. This relates to pore size, particle size and wetting properties of the structure. This is achieved by balancing the relative amounts of binder and catalyst present in the structure.

The purpose of the herein invention is to provide a catalyst composition that is at least as active as the pure platinum one, yet contains less platinum. This results in lower costs, as well as providing superior structural properties at high current density operations.

The electrode of the herein invention comprises a mixture of platinum and silver with the silver constituting more than

half of the catalyst composition on an atomic percent basis. Thus the catalyst composition utilized in this invention will comprise from 20 to 40 atomic percent platinum with the remainder being silver. To indicate the superiority of this composition as an oxygen reduction catalyst, in an electrode having a loading of 20 mg/cm^2 of catalyst where the atomic ratio of platinum to silver is 30:70 there is present 8.6 mg/cm^2 of platinum. Such an electrode containing this amount of platinum, 8.6 mg/cm^2, provides better performance than a similar electrode with a platinum loading of 20 mg/cm^2 and performance equivalent to available electrodes having a platinum loading of 40 mg/cm^2. At higher current densities, above 100 ma/cm^2, less polarization is observed with the catalyst of this invention than is observed for pure platinum electrodes. Thus it can be seen that the herein catalyst at the same loading of catalyst in an electrode will contain significantly less platinum than heretofore has been used yet will produce improved results.

In forming the electrode of the invention, platinum powder, preferably platinum black powder, is blended with the silver powder utilized. In practicing the invention, it is preferred to utilize silver oxide rather than pure silver powder. The amount of silver required in the catalyst mixture is then calculated on the basis of the silver present in the silver oxide. The reason for preferring silver oxide is that pure silver powder does not have a very high surface area. Therefore, it is not as catalytically reactive as desired. Further, since silver is very malleable it tends to form a thin foil when subjected to rolling fabrication processes used to

make the electrodes. On the other hand, silver oxide is not malleable and sinters to a much lesser extent during this operation forming the electrode. Further, the silver oxide has a much finer particle size than typical silver powders.

After blending the platinum with the silver oxide powder, a dispersion of a binder in a large quantity of water is added to the powder and blended thoroughly. A typical preferred binder is tetrafluoroethylene. The excess water is evaporated from the mixture until the mixture has a consistency approximating modeling clay or dough. This doughy mixture is then rolled onto a suitable expanded metal type screen which, for example, can be of nickel, which is gold plated. Such a screen is typically used for electrodes. The material is rolled on to the screen between two thin sheets of inert plastic material such as tetrafluoroethylene films. The formed electrode, which is dried, is then heated at a much higher temperature to sinter the binder material.

In addition to utilizing the aforegoing mixed powders to form the electrodes, it is possible to melt a platinum-silver alloy at the proper composition and forming the required powder, for example, by an exploded wire technique or plasma torch vaporization condensation method. Platinum-silver compositions have, for example, previously been made by the Bureau of Mines.

In formulating the aforegoing electrode the binder weight percent can range from 15 to 40 percent with the remainder being the catalyst. As has been indicated, it is preferred that an inert resinous material be utilized as a binder. Particularly preferred is polytetrafluoroethylene. In addition to

this material, chlorotrifluoroethylene polymers and ethylene/vinyl acetate copolymers such as the Elvax polymers made by E. I. du Pont deNemours can be utilized as binder materials. During the heating operations, the binder material, such as polytetrafluoroethylene is sintered and the wetting agents used to form the dispersion of the resin in water are driven off. As an initial side effect, some of the silver oxide, if such is used, is probably reduced to silver and partially sintered. The remaining silver oxide is reduced electrochemically to silver during fuel cell operation.

The resulting catalyst and electrode formed therefrom is better than an electrode that is obtained with either platinum or silver alone. For example, pure silver electrodes do not show as good a performance for the same loading. Further, a lightweight electrode, which is formed using silver alone loses performance due to sintering which occurs during the fuel cell operation. The initial previous opinion was that platinum is a very good catalyst with a poor structure. However, subsequent theoretical studies indicate that in a tetrafluoroethylene bonded electrode, for example, agglomerates existing in platinum black have an ideal structure to make such a tetrafluoroethylene bonded electrode. However, it appears that platinum may be intrinsically less catalytic for oxygen reduction than silver. Thus it appears that the platinum in the electrode in this invention plays primarily a structural forming role while the silver is a catalyst or at least increases the catalytic activity of platinum. In other words, the two materials peculiarly enhance each other to make both a better structural

electrode and one having improved catalytic properties at the same loading levels of either platinum or silver alone.

It should be pointed out that in order to obtain the same performance as achieved herein with platinum alone, one must utilize, as previously mentioned, a much higher platinum loading and thus incur a much higher price. In addition, an increase in platinum loading does not necessarily mean an equivalent increase in current at a given voltage, because the catalyst utilization becomes poor with increased loading due to the ohmic iR drop across the electrode. Eventually, if the electrode becomes too thick, the catalyst on the back of the electrode is not utilized at all. Thus, further additions of catalyst do not in any way improve performance above a certain limit or thickness. It is believed that the invention will be further appreciated from the following detailed examples.

EXAMPLE

A low temperature alkaline fuel cell was constructed in accord with that shown in the figure. A circular electrode having an area of 50 centimeters squared was prepared by depositing the catalyst on a gold plated expanded metal type nickel frame. The catalyst was prepared by blending 430 mg of platinum black with 612 mg of silver oxide, which was equivalent to 570 mg of silver. 250 mg of tetrafluoroethylene solids dispersed in water was added to the mixture of powder together with a large quantity of water which was then blended thoroughly. The excess water was evaporated until the mixture had a consistency of modeling clay and was then rolled onto

the screen between two tetrafluoroethylene films. The electrode was then dried at 30°C and sintered in a nitrogen atmosphere oven for 15 minutes at 275°C. This provided an electrode having a platinum to silver ratio of 30 to 70 atomic percent. The resulting tetrafluoroethylene bonded electrode had a loading of 20 mg/cm^2 or 8.6 mg of Pt/cm^2. In testing the formed electrode, 35% KOH solution was used in a 30 mil asbestos matrix. The temperature of the cell was 80°C. The hydrogen anode was an American Cyanamid AB-40 anode. The duration of the test was 2275 hours. The electrode of the invention supported a current density of 100 ma/cm^2 at 930 mv and 140 ma/cm^2 at 915 mv vs. hydrogen anode. The aforegoing performance was obtained with a pure platinum catalyst in the same cell utilizing a loading of platinum of 40 mg/cm^2. Thus it can be seen that to obtain the equivalent performance, one had a much higher total loading of catalyst, namely 40 mg vs. 20 of the herein catalyst mixture and more particularly contained about four and a half times as much platinum as used in the catalyst of this invention.