TO:    NIT-44/Scientific and Technical Information Division  
      Attn: Shirley Peigare

FROM: GP-4/Office of Assistant General Counsel  
      for Patent Matters

SUBJECT: Announcement of NASA-Owned U.S. Patents in STAR

In accordance with the procedures agreed upon by Code GP-4 and  
Code NST-44, the attached NASA-owned U.S. Patent is being  
forwarded for abstracting and announcement in NASA STAR.

The following information is provided:

U.S. Patent No. : 4,454,649

Issue Date : 6-19-84

Government or  
Contractor Employee: U.S. Gov't

NASA Case No. : LEW-13653-1

NOTE - If this patent covers an invention made by a contractor  
employee under a NASA contract, the following is applicable:

YES [ ]   NO [x]

Pursuant to Section 305(a) of the National Aeronautics and Space  
Act, the name of the Administrator of NASA appears on the first  
page of the patent; however, the name of the actual inventor  
(author) appears at the heading of Column No. 1 of the  
specification, following the words "...with respect to an  
invention of..."
ABSTRACT

Referring to FIG. 1, a method for making an improved electrode 15 having a gold coating 9 for use in the anode compartment 12 of a REDOX cell 10 is described. The anode fluid utilizes a chromic/chromous couple. The flow chart FIG. 2 illustrates the method wherein a carbon felt is soaked in methanol, rinsed in water, dried and then heated in KOH after which it is again washed in deionized water and dried.

The felt is then moistened with a methanol-water solution containing chloroauric acid and is stored in a dark place while still in contact with the gold-containing solution. After all the gold-containing solution is absorbed by the felt, the latter is dried by heat and then heat-treated at a substantially greater temperature. The felt is now suitable for use as an electrode and is wetted with water or up to 2 molar HCl prior to installation in a REDOX cell.

The two curves on the far right of FIG. 3 illustrate the low hydrogen evolution of the improved electrode.
SOAK IN METHANOL

RINSE IN TAP WATER

DAMP DRY

CLEAN BY HEATING IN 45% KOH

RINSE IN TAP WATER

RINSE IN DEIONIZED WATER

SOAK IN DEIONIZED WATER

DAMP DRY

MOISTEN WITH METHANOL SOLUTION CONTAINING GOLD SALT

STORE IN THE DARK FOR A PREDETERMINED TIME

OVEN DRY

HEAT TREAT

WET WITH WATER

PLACE IN CELL

FIG. 2
HYDROGEN EVOLUTION CHARACTERISTICS OF CHROMIUM ELECTRODES

NOMINAL CAPACITY OF CELLS = 1.075 Amp. Hr.
DATA FROM FIRST CHARGE CYCLE

HYDROGEN EVOLVED DURING CHARGE,

FIG. 3
CHROMIUM ELECTRODES FOR REDOX CELLS

DESCRIPTION

ORIGIN OF THE INVENTION

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

TECHNICAL FIELD

This invention relates to electrochemical cells and is directed more particularly to reduction-oxidation (REDOX) cells.

One of the most highly developed REDOX cells presently known uses an anode fluid having a chromic/chromous couple and a cathode fluid having a ferrous/ferric couple. The anode and cathode fluids are each HCl-water solutions each having the appropriate salt dissolved therein. Electrical potential is obtained from a REDOX cell by means of inert electrodes disposed in the respective anode and cathode fluids.

In general, the electrodes for a REDOX cell must be nonreactive with the anode and cathode fluids while, at the same time, promoting the REDOX reaction on their surfaces. Further, the electrodes must be a porous material which is a good electrical conductor. Graphite foils, cloths or felts are commonly used as electrodes in REDOX cells. A relatively detailed description of the operation and structure of REDOX cells is given in U.S. Pat. No. 3,996,064.

During the operation of a REDOX cell and when the cell is being recharged, hydrogen gas is produced at the electrode in the anode fluid by electrochemical reactions. This results because chromic ion is reduced at a voltage at which hydrogen gas can also be evolved. The extent of the hydrogen evolution depends on the nature of the electrode material.

The chemical reaction of chromous ion, a strong reducing agent, with the hydrogen ion to produce hydrogen gas also takes place but only to a slight extent.

The foregoing hydrogen generating reactions are undesirable because the REDOX cell will eventually attain an imbalance. This imbalance is defined as a different stage of charge in the anode and cathode fluids.

It has been found that silver, copper and gold are all electrochemically active as surfaces for the rapid electrochemical oxidation of chromous ions. While these materials increase the current density available from the REDOX cell, they undesirably increase the amount of hydrogen generated at the anode electrode. The hydrogen evolution at the anode can be reduced by covering the gold, silver or copper layer with a coating of lead as disclosed in U.S. Pat. No. 4,192,910. However, the instant invention achieves additional improvement by other means as will be described presently.

In order for REDOX cells to become generally acceptable, they must be developed to the point where the characteristics of each REDOX cell will be predictable from those of a prototype or pilot model. This has not been possible in the past because it has not been possible to produce gold coated electrodes having reproducible characteristics. Generally, gold coated electrodes made by identical methods have dissimilar characteristics.

treated at a predetermined time and temperature. Before disposing the electrode in the anode fluid of a REDOX cell, it is wetted with deionized water or HCl.

BRIEF DESCRIPTION OF THE DRAWINGS

The details of the invention will be described in connection with the accompanying drawings in which:

FIG. 1 is a schematic drawing of a REDOX system showing the REDOX cell in cross-section.

FIG. 2 is a flow chart of the steps utilized in making an electrode in accordance with the inventive method.

FIG. 3 is a graph comparing the hydrogen evolution characteristics of various electrodes used in the chromous/chromic anode fluid of a particular type REDOX cell.

BEST MODE FOR CARRYING OUT THE INVENTION

Referring now to FIG. 1, there is shown in REDOX cell 10 comprising container 11 which is divided into compartments 12 and 13 by an ion conductive membrane 14. A graphite electrode 15 coated with a thin layer of gold 9 is disposed in the chamber 12 and connected to an output terminal 6. Similarly, a graphite electrode 7 is disposed in compartment 13 and connected to an output terminal 18.

In order to produce a voltage or potential difference between the terminals 6 and 18, a cathode fluid is passed through chamber 13 while an anode fluid is passed through chamber 12. As shown, cathode fluid from a cathode fluid source 19 is circulated by a pump 20 through compartment 13. In the same manner, an anode fluid from an anode fluid source 21 is circulated by a pump 22 through the compartment 12.

The REDOX cell 10 preferably utilizes an iron/chromium system wherein the cathode fluid contains a chromous/chromic couple. The appropriate anode fluid is an aqueous solution of HCl having dissolved therein a chromium chloride salt and a small amount of lead chloride salt. The cathode fluid likewise is an aqueous solution of HCl but has dissolved therein an iron chloride salt. These fluids provide the desired couples in each of the chambers 12 and 13. A more complete discussion of the various REDOX couples, the fluid electrode requirements and membrane considerations is given in U.S. Pat. No. 3,996,064 which is incorporated herein by reference.

In accordance with the inventive method, the steps of which are shown in FIG. 2, a section of commercially available carbon felt approximately one-eighth inch thick and of appropriate electrode size is soaked in methyl alcohol (methanol) for at least 15 minutes, and preferably for approximately 30 minutes. The felt is then rinsed in common tap water and damp dried either by wiping with laboratory wipes such as Fischer Scientific No. 14-206-30 or by being allowed to partially air dry.

Next, the felt is placed in a 30 to 50 weight percent potassium hydroxide (KOH) solution and simmered at a temperature of approximately 100° C. for one to three hours. After being removed from the KOH, the felt is rinsed in common tap water, then soaked in deionized water for at least eight hours after which it is damp dried as discussed previously.

Next, a methanol-water solution which is from 50-80 volume percent methanol is prepared. From 55 to 75 micrograms per milliliter of gold being the preferred amount.

The next step is to moisten the felt evenly by applying the methanol-water-gold solution to both sides at the rate of from about 0.18 to about 0.25 cubic centimeters per square centimeter of felt surface, with the preferred rate of application being about 0.22 cubic centimeters per square centimeter of surface. The moistening is accomplished by determining the projected surface area of the felt electrode and then pouring the required amount of the methanol-water-gold solution into a tray which is inert with respect to the solution and which is large enough to allow the felt electrode to lay flat when disposed therein.

The felt electrode is then disposed in the solution starting at one edge and gradually lowering the whole felt body into the solution. After about two minutes or more, the felt material is carefully turned over and its other side is moistened for the same length of time as the first side was. The solution is worked into the felt, both before and after turning, by pressing all areas of the felt with a suitable flat object.

Because of the time required to completely absorb all the solution in the felt material, the preferred procedure is to pour the solution remaining after the moistening step into a plastic bag, dispose the felt electrode material in the plastic bag and tightly close the bag to prevent leakage. The plastic bag containing the felt electrode and the gold containing solution is then stored in a dark place for a period of from about 10 to about 14 hours at a temperature of from about 0° C. to 35° C. During this time, the remainder of the gold containing solution is soaked up by the electrode and any chemical reaction of the light sensitive gold solution is minimized.

Subsequently, the felt electrode is dried in an oven at about 100° C. for two to three hours. Finally, the felt material is heat treated by placing it in a furnace at a temperature of from about 250° C. to 280° C. for a period of from about two hours to about three hours. The preferred heat treating temperature is between 260° C. and 270° C. The electrode itself is now completed.

As discussed previously, the finished electrode is intended for use in the anode fluid of a REDOX type cell in which the anode fluid utilizes a chromic/chromous couple. Before the electrode is installed in the REDOX cell, it is wetted with deionized water or a 1 to 2 molar HCl solution, which wetting may be accomplished by placing the electrode in a tray containing the solution. For ease of processing, water is normally used.

Referring now to FIG. 3, there are shown curves which illustrate the undesired evolution of hydrogen for electrodes made by four different processes and used in the chromium anode solution of REDOX cells. It will be seen from the curve on the far right that hydrogen evolution is extremely low for an electrode made in accordance with the foregoing described invention.

It will be understood that those skilled in the art to which the invention relates may make changes and modifications to the invention without departing from its spirit and scope as set forth in the claims appended thereto. For example, if the plastic bag in which the electrode is disposed to absorb chloroauric acid is light impervious, it would not be necessary to store the bag in a dark place.

What is claimed is:
A method of making an anode electrode for a REDOX cell comprising the steps, in the following order, of

1. soaking a carbon felt in methanol for at least 15 minutes;
2. rinsing said felt in water;
3. simmering said felt in a 30-to-50 weight percent KOH solution at a temperature of approximately 100°C for 1 to 3 hours;
4. rinsing said felt in tap water;
5. soaking said felt in deionized water for at least 8 hours;
6. drying said felt;
7. moistening said felt with a methanol-water solution which is from 50 to 80 volume percent methanol and which has dissolved therein HAuCl₃·3H₂O whereby all the surfaces of said felt are coated with the gold-containing solution;
8. storing said felt in the dark at a temperature of from 0°C to 35°C for 10 to 14 hours;
9. drying said felt at a temperature of from about 90°C to 130°C; and,
10. heat treating said felt at a temperature of from about 250°C to 280°C for a period of from about 2 hours to about 3 hours.

The method of claim 1 wherein in the moistening step the methanol-water solution has dissolved therein 0.22 cc per square cm.

2. The method of claim 1 wherein the moistening step the methanol-water solution has dissolved therein from 55 to 75 micrograms per milliliter of Au in the form of HAuCl₃·3H₂O and whereby the solution is applied to the felt surfaces evenly in the amount of 0.18 to 0.25 cc per square cm.

3. The method of claim 2 wherein the methanol-water solution is approximately 75 volume percent methanol.

4. The method of claim 3 wherein the dissolved Au in the form of HAuCl₃·3H₂O is in the amount of about 62.5 micrograms per milliliter of solution.

5. The method of claim 4 wherein the methanol-water-HAuCl₃·3H₂O solution is applied to the surfaces of said felt in the amount of approximately 0.22 cc per square cm.

6. The method of claim 5 wherein the felt is maintained at a temperature of approximately 25°C while stored in the dark.

7. The method of claim 5 wherein the drying of said felt after removal from the light-tight container is accomplished at a temperature of about 100°C.

8. The method of claim 5 wherein the heat treating step is carried out at a temperature between 260°C and 270°C for a period of approximately 24 hours.

9. The method of claim 1 wherein the step of soaking said felt in deionized water is over a period of about 10 hours and is preceded by rinsing said felt in deionized water.

10. A method of making a REDOX cell of the type having an ion conductive membrane separating a container into two compartments, one of which contains an anode fluid having a chromic/chromous couple and the other of which contains a cathode fluid having a ferrous/ferric couple, and further including an inert electrically conductive electrode disposed in said anode fluid to develop a negative charge thereon, the method comprising the steps, in the following order, of:

   a. soaking a carbon felt in methanol for at least 15 minutes;
   b. rinsing said felt in water;