United States Patent Office

3,271,195

Patented Sept. 6, 1966

1

3,271,195

ELECTRODES AND METHODS OF MAKING SAME

Aldo S. Berchielli, New Hyde Park, N.Y., and Renato Di Pasquale, Rutherford, N.J., assignors to Yardney International Corp., New York, N.Y., a corporation of New York

No Drawing. Filed July 30, 1962, Ser. No. 213,103
5 Claims. (Cl. 136—67)

This invention relates to electrodes useful in electrochemical devices and to a process for making the same. It also relates to electrochemical devices containing said electrodes.

In the manufacture of electrodes for electrochemical devices, it has been suggested that the electrochemically active metal or a compound thereof, e.g. oxide, hydroxide, in powder form, be pressed in a die to form an electrode plate. In some instances, it has further been suggested that a binder be used to hold the metallic particles of the electrode together.

Electrodes made by these processes leave much to be desired with regard to their mechanical strength. They are generally very fragile and difficult to transport and handle in the various operations that they must be subjected to. Furthermore, these processes are severely limited with regard to the thinness of the electrodes that may be made.

It is an object of the present invention to provide pressed electrodes of the above-mentioned type which have good mechanical strength.

It is another object of the present invention to provide thin pressed electrodes of good mechanical strength, said electrodes being of the order of about below 30 mils thick.

It is also an object of the present invention to provide a process for making electrodes of this type.

It is a further object of the present invention to provide electrochemical devices which have incorporated therein electrodes of this type.

Other and more detailed objects of this invention will be apparent from the following description and claims.

It has now been found that the mechanical strength of these electrodes may be increased by incorporating therein organic or inorganic fibers. The term fiber is used herein in a broad sense in that it is intended to cover any type of a thread-like structure without regard to its particular length.

In carrying out the process of the present invention, the fibers are preferably randomly dispersed in the powdered metal oxides or other metal compounds that are to constitute the electrochemically active materials of the electrode. These fibers are dispersed by preparing a wet slurry with said powders and fibers with or without the aid of binders. In one form of this invention, the resultant mix of fibers and powder is dried, ground and then pressed into a mold. In another form of the invention, the mixture is placed on a carrier, doctored, cut into plates and then pressed. When this powder is compressed, the resultant plate is one which has mechanical stability and great strength because of the mechanical interlocking of the fibers. This process permits the production of a fibrous plate by classical methods of fabrication, such as pressing, rolling, etc. When the fibers are of metallic nature, additional benefit is derived because of the increase of conductivity afforded by the presence of the metal in the resultant electrode.

A variety of fibers may be used in constructing the electrodes of the present invention. These include natural, modified natural, and synthetic organic fibers; natural and manufactured mineral fibers as well as metallic fibers, e.g. fine wire filaments, tinsel threads and metallic wools. These fibers may be used alone or in combination with other types of fibers. Thus, for example, in certain ap-

2

plications, cellulosic fibers such as rayon fibers may be used to advantage in combination with cadmium metal fibers. Furthermore, in some applications, it is advantageous to impregnate fibers with metals, particularly, electrically conductive metals. By way of example, metallic silver may be precipitated in the interstices of a cellulosic fiber such as rayon or silver may be chemically combined with the fiber material in the form of a silver cellulosate.

The following are typical ex imples of fibers that may be used in accordance with this invention: rayon, cotton, nylon, acrylonitrile, cadmium, nickel, zinc, silver, fiber glass, etc.

The quantity of fibers that are incorporated in any given electrode will vary with the particular metal, metal oxide, or other compound employed and the requirements of the electrochemical device. In general, however, this will constitute about between .1% to 5% by weight based on the weight of the electrochemically active material.

As noted above, in one form of this invention, a binder is also incorporated in the electrode. Any of a large variety of binders, well known to those skilled in the art, may be used for this purpose. Of particular usefulness is carboxymethyl cellulose, polyvinyl alcohol or a combination of the two in various proportions. The quantity of binder can also vary, although generally between .1% to 5% by weight of the binder based on the active material, will suffice.

The process of this invention is applicable to the preparation of a variety of metal electrodes. It can, for example, be applied to the preparation of cadmium, silver, zinc, nickel, iron, mercury, etc. electrodes wherein the material used in forming the electrode is in the form of powdered metal or a powdered compound thereof. It has, however, particular application in the preparation of cadmium electrodes wherein the cadmium is utilized in the form of cadmium oxide.

In preparing electrodes of the type herein described, there can also be incorporated therein any of the common additives which are included for the purpose of improving or altering the performance of the electrode. Thus, for example, materials may be added which improve the conductivity of the electrode. Furthermore, materials may be added which reduce the gassing characteristics of the battery or protect the battery on reversal.

The following examples are further illustrative of the present invention. It should be understood, however, that this invention is not limited thereto.

Example 1

Three hundred grams of CdO powder containing 5% nickel powder was formed into a paste with 125 cc. of a .5% aqueous solution of polyvinyl alcohol (viscosity 4–6 cps., hydrolysis 98.5–100%); 125 cc. of a .5% aqueous solution of carboxymethyl cellulose (viscosity 70 cps.) and .5 gram of rayon fibers (¼ inch long, denier 1.5). The paste was air dried at room temperature until a solid product was obtained. This was ground to form particles that passed through an 80 mesh sieve. This powder was placed in a die cavity which was about 1¾ inches wide and 2⅝ inches long and then pressed at room temperature at a pressure of about 10 to 15 tons per in.^{2}. The plate thickness was between 15 to 20 mils.

To complete the electrode, a silver grid made of expanded silver grid material was cut to the approximate size of the plate and a silver tab was welded to one corner of the grid. This was then sandwiched between a pair of plates prepared as described above and the entire assembly was pressed together to form the finished electrode.

Example 2

The procedure of Example 1 was followed except that cotton fibers were used instead of rayon fibers.

Example 3

The procedure of Example 1 was followed except that metallic cadmium fibers of the order of .5 mil thick and up to 1/16–1/4 of an inch long were employed.

Example 4

A solution was first prepared by mixing 60 cc. of a .5% aqueous solution of polyvinyl alcohol and 240 cc. of a .5% aqueous solution of carboxymethyl cellulose. The polyvinyl alcohol was 98.5–100% hydrolyzed and had a viscosity of between 4–6 cps. The carboxymethyl cellulose has a viscosity of 70 cps.

One half of a gram of rayon fibers having a length of about 1/4 of an inch and a denier of 1.5 was placed in the solution prepared above. This mixture was placed in a blender and agitated until a uniform thixotropic suspension was obtained.

Three hundred grams of powdered CdO containing 5% by weight of powdered nickel was added to 300 cc. of said suspension and a slurry was formed. The slurry was placed between 2 layers of carrier paper (Aldex paper) and passed under an oscillating doctor blade to form long strips of electrode material. The strips so formed are air dried at room temperature and the electrode plates of the appropriate size are cut therefrom. The electrode plates are then pressed at a pressure of from about 2–15 tons per in.^{2} to a density of about 20 to 50% (as Cd) of the theoretical density of metallic cadmium. The thickness of the plates were of the order of from 15 to 20 mils.

To complete the electrode, a section of expanded silver grid material was cut to the size of the electrode plate. A silver tab was then welded or otherwise secured to a corner of the grid. The grid now formed was then sandwiched between two electrode plates, prepared as described above, and the whole assembly was pressed together in a press with sufficient pressure so as to form a unitary structure.

Example 5

The procedure of Example 1 was followed excepting that silver oxide powder was used in place of cadmium oxide.

Example 6

The procedure of Example 1 was followed excepting that zinc oxide powder was utilized in place of the cadmium oxide powder.

The electrodes made by Examples 1 to 6 can be used in any of the appropriate silver-cadmium, nickel-cadmium or silver-zinc batteries disclosed in the prior art. Electrodes made by Examples 1 and 4 have, for example, been used in the construction of the batteries disclosed in U.S. Patent No. 2,994,729. They were employed in place of the cadmium electrodes disclosed in said patent. The positive electrodes utilized were sintered silver electrodes which are well known to those skilled in the art (see U.S. Patent No. 2,818,462), with or without an imbedded metallic grid, the silver in the charged state being in the form of silver oxide and or silver peroxide.

The electrolyte utilized was a 30% to 50% aqueous solution of KOH and preferably 40% aqueous KOH. The separator system used is the same shown in said patent, namely a "U" wrap of a semipermeable material such as cellophane, polyvinyl alcohol. The separator system may also contain an ion exchanged.

Whereas the invention has been described with reference to specific forms thereof, it will be understood that many changes and modifications may be made without departing from the spirit of this invention.

What is claimed is:

1. A method of making a composite electrode for a galvanic electrical generator, comprising the steps of:
   (a) forming a viscous mixture of an electrochemically active comminuted material, a resinous binder, and between substantially 0.1 and 5% of said material, by weight, of randomly dispersed reinforcing fibers;
   (b) shaping and pressing said mixture at room temperature into mechanically strong, stable, thin plates; and
   (c) sandwiching a conductive grid provided with an electrode terminal between two of said plates to form an electrode assembly and then pressing the said assembly into a unitary composite electrode.

2. A method of making an composite electrode for a galvanic electrical generator, comprising the steps of:
   (a) forming a viscous mixture of an electrochemically active comminuted material selected from the group consisting of cadmium oxide, zinc oxide and silver oxide, between substantially 0.1 and 5% by weight of said material of a resinous binder selected from the group consisting of carboxymethyl cellulose and polyvinyl alcohol, and between substantially 0.1 and 5% of said material, by weight, of randomly dispersed reinforcing fibers;
   (b) drying said mixture;
   (c) shaping and pressing said mixture at room temperature into mechanically strong, stable, thin plates; and
   (d) sandwiching a conductive grid provided with an electrode terminal between two of said plates to form an electrode assembly and then pressing the said assembly into a unitary composite electrode.

3. The method as defined in claim 2 wherein said fibers are cellulosic.

4. The method as defined in claim 3 wherein said fibers are rayon.

5. The method as defined in claim 3 wherein said fibers are composed of silver cellulose.

References Cited by the Examiner

UNITED STATES PATENTS

2,640,862	6/1953	Chubb	136—67
2,902,530	9/1959	Eisen	136—120
2,977,401	3/1961	Marsal et al.	136—120
3,009,979	11/1961	Corren et al.	136—67
3,013,099	12/1961	Mendelsohn	136—146
3,060,254	10/1962	Urry	136—67

JOHN H. MACK, *Primary Examiner.*

W. VAN SISE, *Assistant Examiner.*