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[54] METHOD AND DEVICE FOR THE MANUFACTURE OF CATALYTIC LAYERS FOR ELECTRODES IN ELECTROCHEMICAL CELLS, PARTICULARLY FUEL CELLS

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[21] Appl. No.: **385,442**

Related U.S. Application Data

[63] Continuation of Ser. No. 142,632, May 12, 1971, abandoned.

[30] **Foreign Application Priority Data**

May 15, 1970 Germany........................... 2023868

[52] **U.S. Cl.**................ **427/115;** 427/189; 427/190; 427/201; 427/282; 136/120 FC; 204/290 F

[51] **Int. Cl.**......................... **B01k 3/04;** H01n 13/00

[58] **Field of Search**......... 117/201, 227, 31, 16, 38, 117/105; 136/120 FC; 156/77; 75/222; 204/290 F, 290 R

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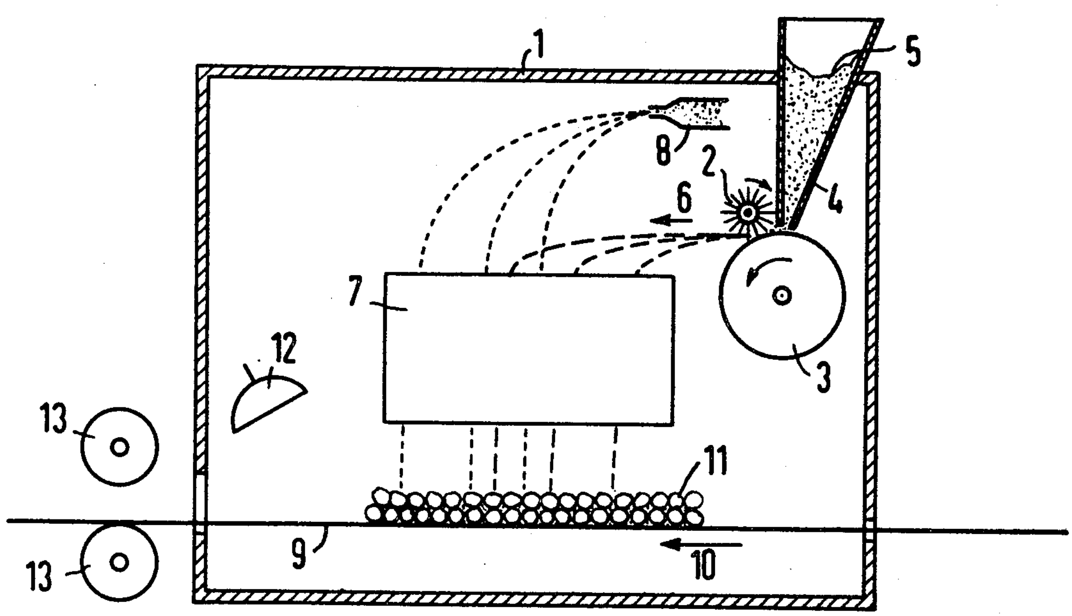
[57] **ABSTRACT**

Method and apparatus for the manufacture of catalytic layers by deposition of a catalyst powder on a substrate comprises the acceleration of the catalyst powder in a direction approximately parallel to the direction of motion of the substrate and the deposition of the catalyst powder with or without a filler onto the substrate under the influence of gravity.

20 Claims, 9 Drawing Figures



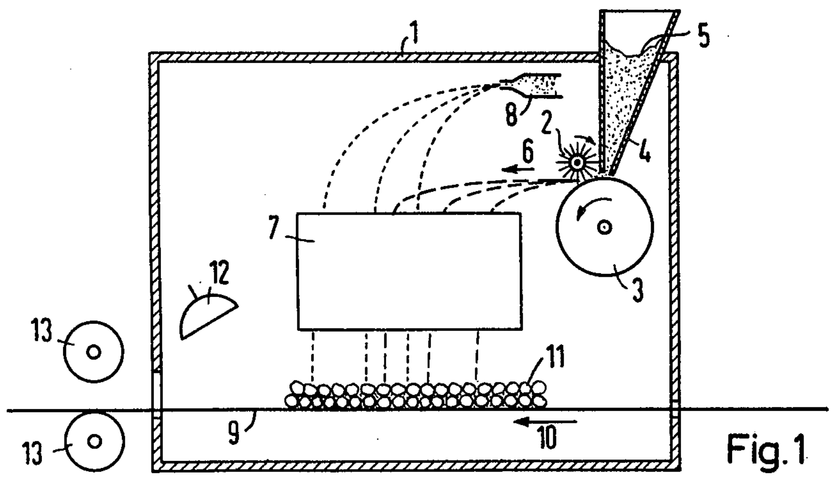


Fig. 1

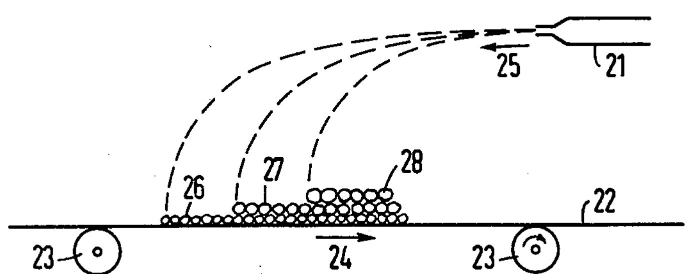


Fig. 2

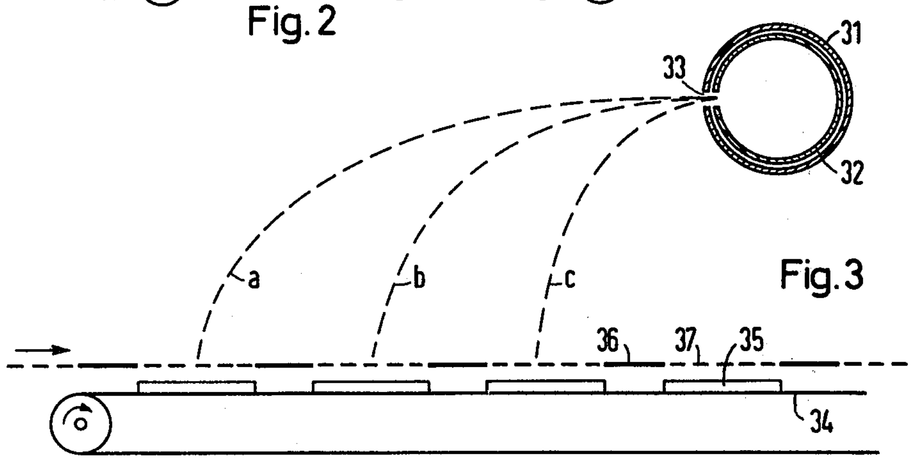


Fig. 3

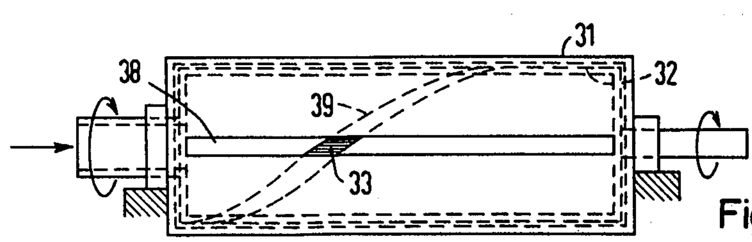


Fig. 3a

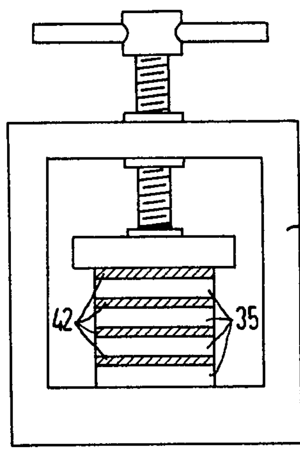


Fig. 4

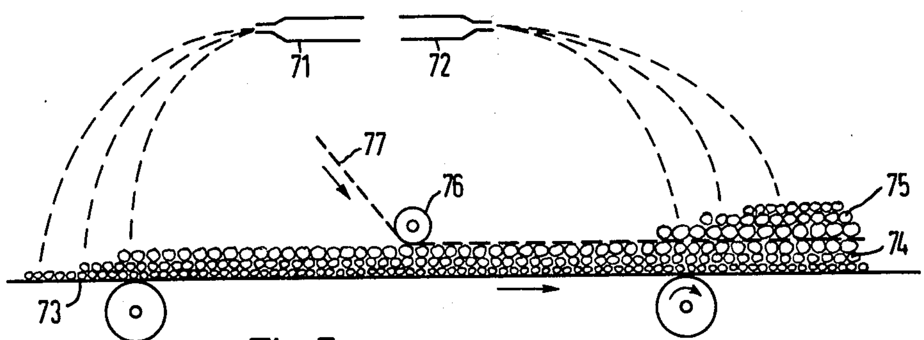


Fig. 7

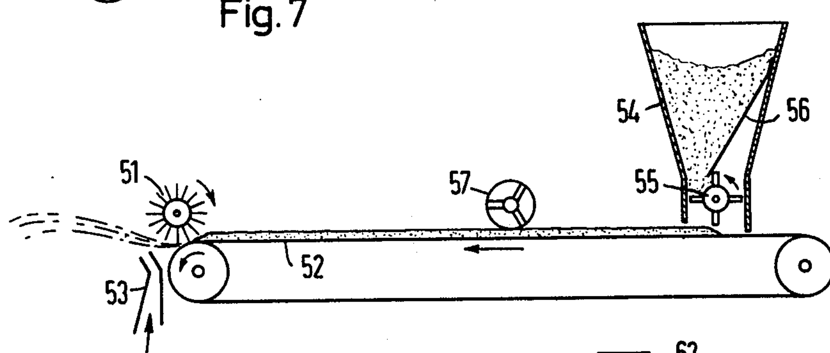


Fig. 5

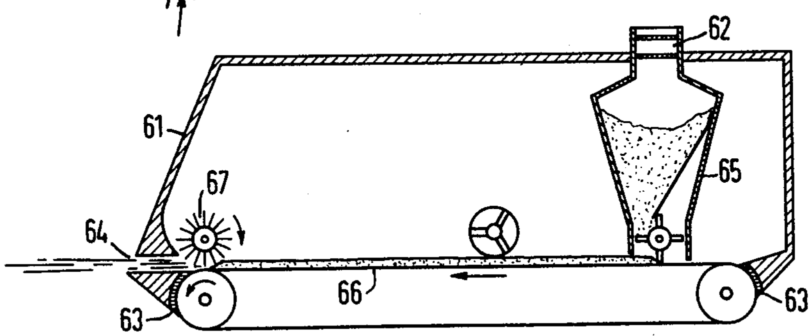


Fig. 6

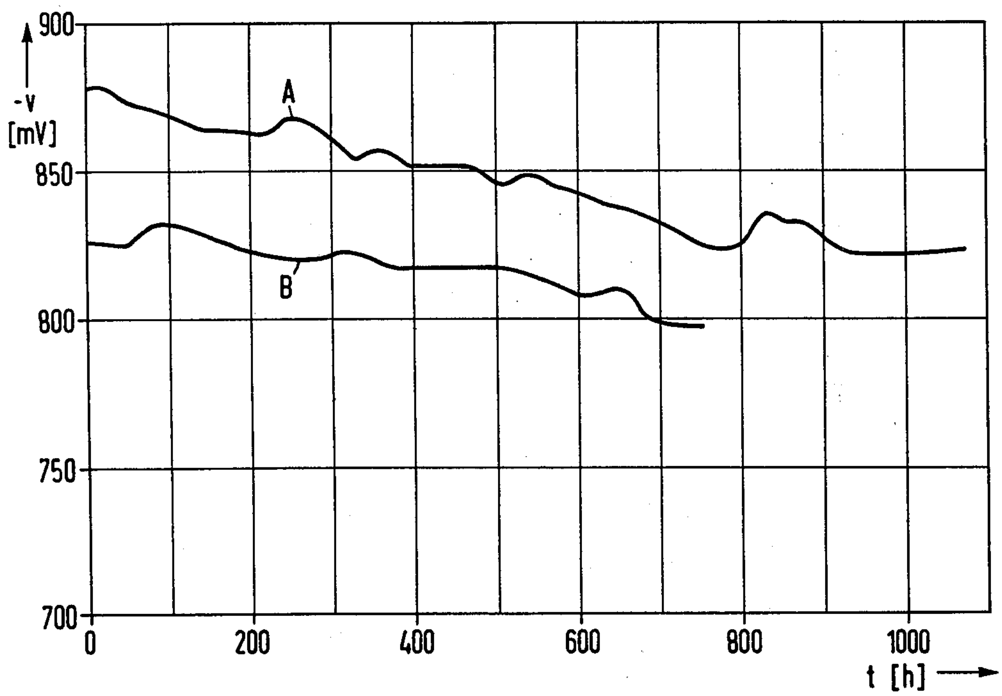


Fig. 8

METHOD AND DEVICE FOR THE MANUFACTURE OF CATALYTIC LAYERS FOR ELECTRODES IN ELECTROCHEMICAL CELLS, PARTICULARLY FUEL CELLS

This is a continuation of application Ser. No. 142,632, filed May 12, 1971, now abandoned.

My invention relates to a method for the manufacture of catalytic layers for electrodes in electrochemical cells, particularly fuel cells, through deposition of a catalyst powder on a substrate under the influence of gravity, as well as apparatus for carrying out this method.

Stringent requirements are placed on the catalytic layers of electrodes for fuel cells with respect to uniform distribution of the catalytic particles in order to obtain a homogeneous pore structure.

According to U.S. Pat. No. 3,226,263, a uniform pore structure is achieved by depositing catalyst powder of a given range of grain sizes through sedimentation in a liquid, for instance, water or glycol, on a solid substrate. The reason for the uniform distribution is found in the relatively slow deposition of the individual grains of the catalyst, whereby the formation of voids and agglomerates is largely prevented. Because of the different sinking velocity of particles of different weight, moreover, fractionization of the catalyst powder by grain size takes place in such a manner that the coarser particles are deposited on the substrate, and the fine particles are subsequently precipitated on top of them. In this manner, catalytic layers can be manufactured, the pore size of which varies uniformly from one layer surface to the other.

With the above-described type of sedimentation, however, there are several shortcomings which make the utilization of the sedimentation process difficult.

In electrodes with a catalyst in powder form, the fine-grained layer, i.e., the most active layer, is adjacent to an asbestos diaphragm which is built into the cell on the electrolyte side. The coarse-grained layer, which is on the gas side, is bounded by a fine-mesh screen, which serves as the gas distributor and current collector. A screen of this kind would now have to serve as the substrate for the sedimentation, unless the entire catalytic layer, after deposition of the catalyst powder, is to be removed from the apparatus and reversed in the sedimentation on another substrate, in which case the obtained uniformity of the catalytic layer can very easily be disturbed again. From the use of the fine screen as the substrate also results the disadvantage that the screen easily becomes warped or curved, which causes the catalyst powder to become detached. Another detrimental effect is that the method is very laborious and not suited for mechanical fabrication. For certain applications, it may furthermore be desirable to obtain a uniform pore structure without sedimentation effect in catalytic layers for electrodes. The known method is also not suited for this purpose.

An object of my invention is to provide a method for the manufacture of catalytic layers by deposition of catalyst powder on a substrate in such a manner that the described short-comings are avoided.

Another object of my invention is to provide a method and apparatus for providing a homogenous catalytic layer by depositing a catalyst powder.

Another object of my invention is to provide such a method and apparatus which is economical to use.

Still another object of my invention is to provide such a method and apparatus which lends itself to easy automation.

Yet another object of my invention is to provide such a method and apparatus which lends itself to the production of catalytic multi-layers from a catalyst powder.

Another object of my invention is to provide such a method and apparatus which produces an electrode having improved characteristics.

Other objects, advantages, and features will become more apparent from the following description.

The above objects are accomplished, according to my invention, in that the catalyst powder is accelerated in a direction approximately parallel to the substrate which is in motion.

The acceleration which is imparted to the catalyst powder has the effect that the latter is distributed uniformly to a high degree. Accumulations are avoided and agglomerations are destroyed. If catalyst powder homogenized in this manner is deposited on a substrate, a catalytic layer is produced with which electrodes can be manufactured that yield very good electrical characteristics. The reason is to be found in the fact that due to the motion of the substrate, a uniformly thin distribution of the catalyst powder takes place at all points of the catalytic layer. Moreover, because the conditions at every point of the area are the same during the deposition of the catalyst powder, a catalytic layer is obtained which exhibits, at every point, a uniform distribution of the grain sizes of the catalyst powder which vary within certain limits, and thereby a uniform composition with regard to the pore structure.

Favorable effects of the method consist furthermore in that correspondingly uniform catalyst layers are obtained also if binders of plastic material, for instance, polytetrafluorethylene, polyethylene or polyglycol, are added to the catalyst powder. Similarly, fillers can be admixed to the catalyst powder, for instance, pulverized, soluble salts such as potassium carbonate and potassium oxalate. These pore fillers can also be contained in the catalyst powder particles themselves, i.e., impregnated catalyst powder can be used. This can be achieved by treating the catalyst powder with solutions of these salts and subsequent drying.

An advantageous form of carrying out the method for the manufacture of catalytic layers consists in that catalyst powder of different grain sizes is used, and that it is additionally aerated by means of a stream of gas. This can be accomplished advantageously by blowing air through a nozzle against the accelerated catalyst powder or by blowing the catalyst powder through a nozzle by means of air, in which case the acceleration and the aeration take place together.

Through the acceleration in conjunction with additional aeration of the catalyst powder of different grain sizes, a sedimentation effect is achieved. This is to be understood in the sense that through the action of the gas stream the catalyst powder particles of different size and weight are carried different distances and that through the effect of gravity different trajectories result therefrom. As the substrate is further moved, strata with different grain sizes are produced within the catalytic layer during the deposition of the catalyst powder. This, in turn, means that, in addition to the uniform distribution of the catalyst powder over an extended area, which is caused by the acceleration of the material, a distribution is obtained within the layer in such a manner that the grain size of the catalyst granules decreases or increases uniformly. With this gradation of the catalyst powder by grain size, a pore structure is achieved in which the pore size changes uniformly between the two surfaces of the layer, i.e., the pores either become smaller or larger.

In this connection, an additional advantageous effect is realized in that a substrate which is in motion is used for the deposition of the catalyst powder. If the direction of the acceleration of the catalyst powder and the direction of the motion of the substrate are the same, the particles with the largest grain size are deposited first, and subsequently for finer particles. If, however, the acceleration of the catalyst powder is opposite to the direction of motion of the substrate, gradation in the opposite sense takes place: the catalyst particles of large grain size come to rest on top of the particles with smaller grain size. It is thereby possible to deposit the catalyst powder directly on diaphragms used for the manufacture of the electrodes, or directly into cell frames. To this end the substrate, which advantageously is made as a carrier belt, can be a conveyor belt on which the plate-shaped parts used to receive the catalyst powder are arranged, the dimensions of which correspond to the size of the electrodes and which can be designed as cell frames. The diaphragms used can be wetted, if desired, to obtain good adhesion.

Those parts of the substrate which are not to be coated can be masked. This, however, can also be achieved through the use of an endless foil into which the masks have been worked.

The coated plate-shaped parts can be stacked and subjected to a pressing operation in a suitable manner. If the substrate is developed as a carrier belt, the latter can be fed through the rollers of a calender after coating with the catalyst powder in order to give the catalytic layer additional strength. If desired, a contact grid can at the same time be worked into the catalytic layer. Subsequently, the electrodes can be blanked out and assembled in the cell frames.

The pressing operation is of particular advantage if a binder has been added to the catalyst powder or if in addition to the catalyst powder, the binder has been applied to the substrate by means of an additional nozzle. This additional nozzle can also be used for applying the filler.

To carry out the method, a device according to my invention comprises feeding, transporting and accelerating means located above an endless, movable carrier belt for the material to be deposited.

The acceleration of the catalyst powder can be accomplished by a mechanically moved device. A rotating brush may be advantageously used for this purpose. If the accelerating is done by means of a nozzle, the latter is moved transversely to the direction of motion of the substrate.

Through the combination of acceleration and deposition of catalyst powder, catalytic layers are produced which have important structural characteristics. The uniform distribution of the catalyst material over a large area makes it possible to manufacture electrodes which exhibit very good electrical characteristics. The additional aeration prior to the deposition on the moving substrate permits, by using catalyst material of different grain sizes, the manufacture of catalytic layers which, besides having a homogeneous structure, exhibit additionally a gradation of grain sizes, which is equivalent to a continuous increase or decrease of the pore size across the strata of the catalytic layer. Further advantages accrue from the fact that the preparation of the catalytic layers takes little time and that the method is highly suitable for mechanized mass production.

The invention will be further described with reference to embodiments thereof, illustrated by way of example on the accompanying drawings in which:

FIGS. 1 to 3 are views of different embodiments of apparatus for performing the method according to my invention;

FIG. 3*a* is a cross-sectional view along lines 3*a*—3*a* of FIG. 3;

FIG. 4 is a view illustrating an embodiment of a device for pressing of the plate-shaped parts;

FIGS. 5 and 6 are views of still further embodiments of apparatus for carrying out my method;

FIG. 7 is an illustrative view of apparatus for the manufacture of multi-layer electrodes; and

FIG. 8 is a graph of the potential at the two electrodes versus time.

Referring to the drawings, and in particular to FIG. 1, the apparatus for performing the method of my invention is provided with a housing **1**, The acceleration means of my invention consists of a rapidly rotating brush **2**, the bristles of which contact the outer surface of a cylinder **3**, which serves as a transport means. The diameter of cylinder **3** is larger than the diameter of the brush **2**, and brush **2** and the cylinder **3** move in opposite directions. A downwardly tapered container feeding means **4** tapers toward the cylinder **3**, and is provided at its tapered lower end with a slit the length of which approximately corresponds to the length (in the axial direction) of the brush **2**. In the feeder or hopper **4** is the catalyst powder **5**, for instance, a free-flowing powder such as Raney silver. The catalyst powder **5** is accelerated in the direction indicated by arrow **6** and falls between partitions **7**. Several such partitions are arranged parallel to each other, and they delineate at least a part of the trajectory of the catalyst powder suppressing turbulence transversely to the direction of acceleration. A nozzle **8** is provided above the flow of the catalyst **5** and serves to apply a filler and/or binder material to a carrier belt **9** serving as the substrate **9** upon which the catalyst powder is deposited. The binder could be a suitable plastic material. The direction of motion of the substrate or carrier belt **9** is indicated by the arrow **10**.

As a result of the movement of the catalyst powder, a uniform catalytic layer **11** (enlarged) is deposited on substrate **9**. As the substrate moves, it passes a drying device **12**, for instance, an infrared radiator. Drying is advisable, particularly if moist materials are used. For additional drying purposes, a tunnel oven section can also be utilized, if desired. In order to obtain a further solidification of the catalytic layer, the coated substrate can be fed through cylinders **13** of a calender located above and below the substrate **9**. If required, a contact grid additionally can be included at this point. Subsequently, the electrodes are blanked out and mounted into the cell frames.

FIG. 2 is another embodiment of my invention, in which the catalyst powder of differing grain size is simultaneously accelerated in a horizontal direction and aerated by means of a gas stream through a nozzle **21**. For practical purposes, air is used. The nozzle **21** has a suitable opening, for instance, of annular cross-section, and is moved transversely to the direction of motion of the substrate 22 to apply a uniform layer across the width thereof. The velocity of motion of the nozzle, which is fast compared to the velocity of the substrate, is essentially constant over the entire width of the substrate. In FIG. 2 the carrier belt is 22 and it is carried over rollers **23**. The direction of motion **24** of the carrier belt is opposite to the direction of the acceleration **25** of the catalyst powder emanating from nozzle **21**, so that the fine catalyst powder particles **26** are deposited first. The particles **27** of medium grain size and the coarse particles **28** settle out subsequently. If the direction of motion of the belt **22** is the same as that of the acceleration, an inverse grading of the catalyst powder particles is obtained.

In the embodiment illustrated in FIG. **3**, the acceleration means consists of two concentric tubes **31** and **32**, which at the same time accelerate and aerate the catalyst powder. The outer tube **31** is fixed while the inner tube **32** rotates. The catalyst powder is fed to the inner tube axially by means of air. The catalyst powder leaves the accelerating means through an opening **33** in the inner and outer tubes when their respective openings are in registry. The conveyor belt **34** moves in a direction which is opposite to the direction of acceleration of the catalyst powder. A plurality of plate-shaped parts or cell framed **35** onto or into which the catalyst powder is deposited are carried by conveyor **34**. The distribution of the catalyst powder particles of fine, medium and coarse grain size is designated by a, b and c, respectively. Masks **36** are worked into a foil **37**, as indicated by dashed lines. The foil can be also an endless belt. The direction of motion and the velocity of the foil and conveyor belts are the same. By deflecting the endless foil belt, the catalyst powder lying on it is thrown into a storage bin.

FIG. 3a shows the accelerating means of FIG. 3 consisting of the two concentric tubes in cross-section. The outer, fixed tube **31** has a narrow, straight slit **38** which extends almost over the entire length of the tube. The inner, rotating tube **32** has one or several spirally arranged slits **39**. Due to the rapid rotation of the inner tube the opening **33** is continuously shifted, and clogging of the slit **38** is prevented by this arrangement. The speed of rotation of the inner tube is sufficiently large in relation to the velocity of the substrate.

Referring now to FIG. **4**, the plate-shaped members **35**, which are covered with catalyst powder **42**, have their dimensions corresponding to the size of the electrodes, and are taken off the conveyor belt **24**, stacked and, as shown in FIG. **4**, pressed in a suitable housing **41**.

FIG. 5 illustrates another embodiment of this invention, in which the acceleration means are a rotating brush **51** pushing the catalyst powder off a conveyor belt **52** which transports the catalyst powder slowly against the rotating brush. Through a nozzle **53**, a stream of gas blows on the accelerated catalyst powder and aerates it as it accelerates. It is desirable to use air for this purpose. The feeding means used to apply the catalyst powder to the conveyor belt **52** consists of a tapered supply tank or hopper **54** and a rotating conveyor roller **55** provided with radial arm members. The conveyor roller **55** continuously hits a movable wall **56** with its arm members, whereby the catalyst powder is vibrated and can thereby be applied to the conveyor belt more uniformly. A distributor worm member **57** smoothes the applied catalyst powder out. It is advisable that this is done if catalyst powder is used to which binder is admixed.

FIG. 6 shows another embodiment of my invention, in which the feeding, transport and acceleration means, i.e., in this case, the supply tank **65**, the top side of the conveyor belt **66** and the rotating brush **67** are located in a tank **61** which is under gas pressure. The catalyst powder is brought into the supply tank **65** via an air lock mechanism **62**. The conveyor belt **66** is sealed against the housing **61** by means of rubber or polytetrafluorethylene layers **63**. The catalyst powder and the gas, preferably air, leave through a slit **67** acting as a nozzle in the wall of the housing between the brush **64** and the conveyor belt **66**, i.e., between the transport and the acceleration means.

In accordance with the embodiment of FIG. **7**, it is possible to manufacture a double-layer electrode by providing two acceleration means. In this case, two nozzles **71** and **72** are used as acceleration means. Acceleration and aeration of the catalyst powder is achieved simultaneously as described above with reference to FIG. **2**, and, when using catalyst powder of different grain sizes, catalytic layers are obtained which exhibit a homogenous composition as well as a gradation of grain sizes. With the nozzle **71**, a catalytic layer **74** is produced; the direction of acceleration of the catalyst powder is opposite to the direction of motion of the carrier belt **73**, while the acceleration of the catalyst powder by the nozzle **72** is in the same direction as the direction of motion of the carrier belt **73**. A catalytic layer **75** is produced thereby, the grain gradation of which is a mirror image of the gradation of the catalytic layer **74**. By means of a suitable device, for instance, a roller **76**, a screen **77** is inserted between the two catalytic layers **74** and **75** to create a hollow space which can, for instance, serve as the gas space of a double-layer electrode. Through arranging several acceleration means, multi-layer electrodes can also be made which exhibit a homogeneous structure in the individual catalytic layers. Here, catalyst powders of different materials can be applied through the individual acceleration means. When using catalyst powders of different grain sizes, different gradation in the individual catalytic layers can moreover be achieved through the use of nozzles as acceleration means, depending on the direction of the acceleration of the catalyst powder relative to the direction of motion of the carrier belt.

FIG. **8** is a graph of the potential of two electrodes A and B versus time. On the ordinate is plotted the potential $-v$ in mV, while on the abscissa, the time in hours. In electrode A, a catalytic layer was used which was made in accordance with my invention and which exhibited a homogeneous structure. In detail, the catalyst powder has been accelerated with a brush, deposited on plate-shaped parts and subjected to a pressing operation. The pressure was approximately 10 kg/cm^2. For the preparation of electrode B, the catalyst powder was sprinkled on a substrate and rolled out manually with a roller. Both electrodes were of approximately 290 cm^2 and about 0.8 mm thick. They had a coating of approximately 200 mg of material per cm^2. As catalyst powder, Raney nickel with a grain size of less than 40 μ was used; it contained in each case about 4.5% polytetrafluorethylene as binder.

The voltage v of the electrodes against an Hg/HgO standard cell was determined with a load of 80 mA/cm^2. 6 n KOH at 60° was used as the electrolyte and the hydrogen pressure was 1.46 atm.

It is found that electrode A yields a voltage about 50 mV higher than electrode B at the start, and after 500 hours of operation, the voltage of A is still about 30mV higher. This means that a higher cell voltage is obtained with electrode A than with electrode B over the entire test period of more than 1,000 hours.

Especially in the case of a hydrogen electrode, this improvement is of decisive importance, as here the electrode must be operated above a critical potential which, for the commonly used nickel electrodes, is at about −780 mV against Hg/HgO. At this critical potential, destruction of the electrode due to irreversible oxidation takes place. The shape of the characteristic for electrode A shows that it can be operated for a very long period above this critical potential at high current density.

The test result demonstrates that with the electrode manufactured according to my invention, electrical characteristics can be achieved which are of interest for the construction of fuel cells. The reason for the improvement of the electrical characteristics is found to be the described uniform distribution of the catalyst powder in the catalytic layer, which can also be seen from photomicrographs.

In addition to fuel cells, the electrodes manufactured according to my invention can also find application in other electrochemical cells, for instance, in electrolyzers.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in the above method and apparatus without departing from the scope of the invention, it is intended that all matter contained in the above description and shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

I claim:

1. Method for the manufacture of porous catalytic layers for electrodes in electrochemical cells, especially fuel cells, from catalyst powder of different grain sizes which comprises moving a planar substrate generally along a predetermined and generally straight line path, aerating said catalyst powder of different grain sizes with a gas stream, accelerating and directing a stream of catalyst powder initially in a direction substantially parallel to said straight line path and disposed above said moving substrate, whereby the catalyst powder particles of different size and weight are carried a different distance, and utilizing the effect of gravity to cause said stream of catalyst powder to fall by gravity onto said moving substrate thereby to form a planar layer on the substrate with gradation of the catalyst powder forming the planar layer by grain size and in which the pore structure of said planar layer has pore size changes with smaller pores with the smaller grain particles and with the pore sizes increasing with the larger size particles.

2. Method according to claim 1, wherein said step of directing a stream of catalyst powder comprises passing said gas stream through a nozzle and blowing said gas stream at the catalyst powder.

3. Method according to claim 1, wherein said step of directing a stream of catalyst powder comprises directing said stream in the direction of motion of the substrate.

4. Method according to claim 1, wherein said step of directing a stream of catalyst powder comprises directing said stream opposite to the direction of motion of the substrate.

5. Method according to claim 1, which comprises admixing to the catalyst powder a binding agent of plastic material.

6. Method according to claim 1, which comprises admixing to the catalyst powder a filler.

7. Method according to claim 3, wherein the filler is contained in the particles of catalyst powder.

8. Method according to claim 1, comprising simultaneously accelerating and aerating the catalyst powder.

9. Method according to claim 8, comprising blowing said catalyst powder from a nozzle by means of a gas.

10. Method according to claim 9, wherein said gas is air.

11. Method according to claim 9, comprising moving the nozzle through which the catalyst powder is blown transversely to the direction of motion of the substrate.

12. Method according to claim 1, comprising applying a filler to said substrate by means of a nozzle.

13. Method according to claim 1, comprising applying a binding agent to said substrate by means of a nozzle.

14. Method according to claim 1, wherein said substrate comprises a carrier belt.

15. Method according to claim 14, comprising moving said carrier belt with the deposited catalyst powder through a calender.

16. Method according to claim 1, wherein said substrate comprises plate-shaped parts, and carrying said plate-shaped parts on a belt, said plate-shaped parts having dimensions corresponding to the size of the electrodes.

17. Method according to claim 16, comprising forming said plate-shaped parts as cell frames for electrodes.

18. Method according to claim 16, comprising masking said plate-shaped parts by masks.

19. Method according to claim 18, comprising working said masks into a foil, said foil being an endless belt.

20. Method according to claim 16, comprising stacking said plate-shaped parts together with the deposited catalyst powder and pressing the stacked plate-shaped parts and deposited catalyst powder.

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