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Method for producing gas diffusion electrodes

The invention relates to a method for producing gas diffusion electrodes which consist at least of an electrically conductive catalyst support and a sheet-like structure produced by rolling a powder mixture. The powder mixtures contain at least one catalyst or a catalyst mixture and a binder.

DE-A 37 10 168 and EP-A 297 377 describe the production of gas diffusion electrodes by rolling dry powder mixtures containing a compound of the catalyst material, for example silver(I) oxide, and polytetrafluoroethylene (PTFE) as a binder. After the rolling of the powder mixture to give a sheet-like structure, the latter is applied to or rolled in a mechanical support which serves for supplying current to or conducting current away from the electrode. The mechanical support may be, for example, a metal net, nonwoven metal fabric or woven metal fabric or a carbon net, nonwoven carbon fabric or woven carbon fabric. The application of the sheet-like structure to the mechanical support can be effected, for example, by pressing or rolling.

The properties of the sheet-like structures which are produced by rolling the powder mixtures are dependent on a multiplicity of parameters. In addition to the powder characteristics themselves, these parameters include, inter alia, the geometry and the surface characteristics of the rolls, the speed of the rolls, the precision of the bearings used, the truth of running of the bearings on the one hand and of the rolls on the other hand, the roll nip and the clamping force of the rolls. If, for example, the roll nip varies greatly during the rolling process, in particular sheet-like structures whose thickness and density are not sufficiently homogeneous are obtained. If, on the other hand, the roll nip is kept substantially constant, in particular by an excessively high clamping force, the electrodes exhibit, inter alia, very disproportionate voltage increases with increasing current density and poor electrochemical activity during operation. Furthermore, excessively thick and mechanically unstable sheet-like structures cannot be used for further processing. Regarding the technical handling properties, for example for use as gas diffusion electrode for the electrochemical production of chlorine from aqueous solutions of alkali metal chloride, such sheet-like structures must have a length of from 2 to 3 meters and a width of from 30 to 40 cm.

For stability reasons, commercial rolls having a width of about 40 cm have diameters



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of about 15 cm or more, depending on the maximum clamping forces to be applied. It was found that sheet-like structures which were produced with such rolls and were used as gas diffusion electrodes did not have sufficient electrochemical activity. This greatly increases, in particular, the operating costs of electrolysis cells and the like.

5 The electrochemical activity is insufficient, for example, if the electrode has a cell voltage of over 2.5 V at a current density of 4 kA/m².

It is an object of the invention to provide a method for producing gas diffusion electrodes, by means of which electrochemically active sheet-like structures having

10 high homogeneity of the density and small thickness variations can be produced. The gas diffusion electrode must furthermore have good electrochemical activity and mechanical stability. The parameters of the rolling process must be chosen so that, during rolling of the powder mixture to give a sheet-like structure, optimum electrochemical activity is achieved and said activity is not adversely affected during

15 application of the sheet-like structure to the catalyst support by rolling.

The object is achieved, according to the invention, by the features of claim 1 or 2 or 3.

20 In a first preferred embodiment of the method according to the invention, the sheet-like structure is produced by rolling a powder mixture which contains at least one catalyst or a catalyst mixture and a binder. According to the invention, the clamping force of the rolls is kept constant in the range from 0.2 kN/cm to 15 kN/cm during the rolling process of the powder mixture. It is particularly preferable to provide a

25 clamping force in the range from 0.2 kN/cm to 10 kN/cm, preferably from 0.2 kN/cm to 5 kN/cm and particularly preferably from 0.2 kN/cm to 2 kN/cm. Particularly good results were obtained when the clamping force was kept in the range from 0.3 kN/cm to 0.6 kN/cm.

30 The clamping force can be generated hydraulically and/or mechanically and/or pneumatically. This has the advantage that the clamping force is very exactly adjustable.

In a second preferred embodiment of the method according to the invention, rolls

35 whose diameter is not less than 8 cm and not more than 15 cm, preferably not more than 13 cm and particularly preferably not more than 11 cm are used.

In a third preferred embodiment of the method according to the invention, the sheet-like structure produced by rolling is also connected to an electrically conductive support by rolling. Rolling is effected under a nip force of from 0.1 kN/cm to 2 kN/cm.

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A combination of the three preferred embodiments of the method according to the invention is particularly preferred.

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A substantial element of the invention is that a lower clamping force must be applied during rolling in the case of a smaller diameter of the rolls. Thus, there is only one specific operating range for each roll diameter with regard to the clamping force and the resulting thickness and density of the sheet-like structure. For example, it is not possible to produce a sheet-like structure having a thickness of 0.35 mm and a density of 4.4 g/ml using a roll diameter of 13 cm and a clamping force of 1.5 kN/cm. This is possible only in the case of a smaller roll diameter.

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It was surprisingly found that, under the conditions according to the invention for rolling the powder mixture, sheet-like structures are obtained from which electrodes having sufficient mechanical stability and electrochemical activity can be produced.

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The sheet-like structure for gas diffusion electrodes which is produced with the aid of the method according to the invention has high homogeneity. It is possible to achieve density variations which are in the range from ± 0.2 to ± 0.5 g/m³. Furthermore, it is possible with the aid of the method according to the invention to produce sheet-like structures whose thickness variations range from ± 0.05 mm to ± 0.2 mm.

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The electrochemical activity of the electrode is to be understood as meaning, in addition to the voltage at a specific current density, the change in the voltage at higher current densities and the gas and liquid permeability during operation. With a good electrode, the electrolysis can be operated at high current densities and low voltage, and the increase in the voltage on increasing the current density is only small. Thus, for example, the electrolysis of a sodium chloride solution, in which chlorine is evolved at the anode and oxygen is consumed and sodium hydroxide solution is formed at the cathode, can be operated at a current density of 4 kA/m² with a voltage of less than 2.5 V. Ideally, the electrode allows no gas to pass through from the gas side into the liquid space and, conversely, no liquid into the gas space.

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The preferably dry powder mixture for the material of the sheet-like structure may consist of a binder, for example a polymer, such as polytetrafluoroethylene (PTFE), a catalyst or a catalyst mixture. It is also possible for one of the components of the powder mixture to be carbon or a carbon-containing compound. The powder mixture
5 may also contain additives, such as, for example, ammonium bicarbonate, which acts, inter alia, as a pore former. The catalyst or the catalyst mixture may consist, for example, of nonmetallic compounds of a metal forming the catalyst or of mixtures of metal and of the nonmetallic compounds of a metal forming the catalyst. It is also possible to use mixtures of different metals or metal compounds, preferably noble
10 metals. Silver(I) oxide or mixtures of silver(I) oxide and silver metal is or are preferably used as the catalyst. A Teflon powder from DYNEON, type 2053, is preferably used as the binder. The mixture of binder and catalyst or catalyst mixture can be milled, for example, as described in DE-A 2 941 774, using a high-speed mill with beater knives. The moisture content of the powder mixture is not more than
15 0.5% by weight of H₂O, preferably not more than 0.3% by weight of H₂O.

The rolling of the powder mixture can be effected using commercial roll shells, as used in the production of such sheet-like structures or in the compacting of powders. The individual rolls may have different diameters. It is also possible for the rolls to
20 run at different speeds. The roll surfaces should have a roughness at which the powder mixture can still be drawn in at uniform speed. The aim is to produce a homogeneous sheet-like structure. The surface roughness of the roll can be adapted according to the property of the powder mixture. Smooth roll surfaces are preferably employed, i.e. surfaces which do not have a coarse structure. The surface roughness
25 of the roll, measured as the Ra number, is preferably between 0.05 μm and 1.5 μm .

Further parameters which may influence the draw-in behavior of the powder mixture, in addition to the properties of the powder mixture itself, are, for example, the speed of the roll or the roll nip set or the combination of a plurality of parameters.

30 The rolling of the dry powder mixtures is carried out in such a way that the distance between the two rolls is adjusted to a specific value, e.g. 0.2 mm, before the rolling process. The roll nip set should be chosen according to the powder characteristics, the surface roughness of the rolls, the speed of the roll and the diameter of the roll, so
35 that the sheet-like structure produced has a thickness of from 0.05 to 0.7 mm. The thickness of the sheet-like structure is preferably from 0.15 to 0.6 mm. Depending on the powder and on the powder characteristics, the roll nip for achieving the above

thicknesses of the sheet-like structure is preferably from 0 to 0.30 mm, in particular from 0.005 to 0.2 mm. Thereafter, the dry powder mixture is metered onto the roll nip, and the roll draws in the powder and compacts it to a sheet-like structure. Since, according to the invention, the clamping force is kept constant during the rolling process, the preset roll nip expands slightly on drawing in the powder material and varies slightly during the rolling process, depending on the amount and characteristics of the powder material drawn in. The roll nip varies in a range from ± 0.05 to ± 0.2 mm.

For carrying out the method according to the invention, it is advantageous if the bearing play of the bearings holding the rolls is small, i.e. if the bearings used have a bearing play of, preferably, less than 0.06 mm and a truth of running of less than $50\text{ }\mu\text{m}$ and if the rolls preferably originate from a production series in whose production extremely high precision was ensured. This applies not only to the bearing play of the bearings and bearing blocks used but preferably also to parts in which the bearings are mounted in the roll stand, if they influence the roll nip.

If the sheet-like structure is connected to an electrically conductive support by the method according to the invention, on the one hand the sheet-like structure is connected to the support so firmly that it has low-resistant contact with the support and can no longer be detached therefrom and, on the other hand, the pore system of the sheet-like structure is not destroyed, so that sufficient electrochemical activity is ensured. The electrically conductive support is, for example, a metal net, a nonwoven metal fabric, a woven metal fabric or a metal foam. Expanded metals may also be used. The support preferably consists of nickel or nickel-plated metal compounds or nonmetal compounds, for example carbon. The support performs the function of a current distributor.

The application of the electrochemically active sheet-like structure to the electrically conductive support could be effected, for example, also by pressing. However, rolling has the advantage that the gas diffusion electrode can be produced in a continuous process and the forces are uniformly distributed. The force which is applied during rolling depends on the support. The greater the mesh size of the metal net and the smaller the thickness of the metal wire, the lower the force required. The same applies to expanded metals, in which the required force decreases with increasing mesh size and mesh width but decreasing web thickness.

In a preferred embodiment, the electrically conductive support is connected mechanically and in an electrically conductive manner to a gas-permeable, metallic baseplate, in order in particular to ensure the mechanical stability of the gas diffusion electrode. The baseplate consists in particular of nickel or of a nickel alloy, e.g. a nickel-silver alloy. It has a multiplicity of orifices, for example slots or holes, for passing through the reaction gas. The more stable the support or the support provided with a baseplate, the greater the extent to which it is deformed during the rolling process. The deformation can be avoided or reduced if, preferably, different circumferential speeds are chosen for the two rolls.

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The temperature of the sheet-like structure and/or of the electrically conductive catalyst support during the rolling process is preferably from 5 to 70°C. In order to maintain this temperature range, thermostatable roll shells are preferably used. The roll shells are hollow for the passage of a cooling or heating medium. It is particularly preferable if the rolls are cooled during the rolling process, since the powder compaction heats up the powder due to frictional forces. The rolls may optionally also be heated at the beginning of the rolling process for reaching the operating temperature or may be thermostated at an elevated temperature. If the roll shells are produced from solid material and cannot be thermostated, the powder mixture to be rolled must be brought to the desired temperature before the rolling process.

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The speed of the roll is freely selectable within certain ranges, provided that the powder is drawn in homogeneously by the rolls. Particularly preferred, however, are circumferential speeds of the rolls which are in the range from 0.05 to 19 m/min, in particular from 0.1 to 15 m/min.

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The gas diffusion electrodes produced by the method according to the invention can be used in an electrolysis process, in particular in the electrolysis of an aqueous solution of sodium chloride.

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The sheet-like structures for a gas diffusion electrode which were produced according to the following examples were used in the chloralkali electrolysis. A cell which consisted of an anode space and, separated by an ion exchange membrane, a cathode space was used for this purpose. A sodium chloride solution which had a concentration of 200 g/l and was reacted to give chlorine at a ruthenium oxide-coated titanium electrode was used in the anode space. The cathode space was separated

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from the anode space by a cation exchange membrane from DuPont, type Nafion[®] 982. Between gas diffusion electrode and cation exchange membrane was an electrolyte gap in which an approx. 32% strength sodium hydroxide solution was circulated by pumping. Behind the gas diffusion electrode, pure oxygen having a
5 content of 99.9% was passed into the cathode half-cell. Anode area, membrane area and gas diffusion electrode area were each 100 cm².

Example 1 (Comparative example)

A mixture of silver(I) oxide and PTFE in the weight ratio 9:1 was milled by means of a high-speed beater mill, from IKA, type M20, at intervals of in each case 15 seconds with cooling. This mixture was rolled on a roll mill from Wetzels, comprising 2 roll shells having a width of 40 cm and a diameter of 13 cm with a roll nip of 0.18 mm over a width of 20 cm at a clamping force of 0.075 kN/cm. The circumferential speed was 1.35 m/min and the roughness of the roll surfaces had a Ra number of 25-30 μm . The temperature during the rolling process was 22°C. The sheet-like structure obtained had a thickness of 1.1 mm and was mechanically very unstable. The sheet-like structure could not be applied without destruction to a mechanical support, a nickel net having a nickel wire thickness of 0.14 mm and a mesh size of 0.5 mm. Production of a gas diffusion electrode was therefore not possible.

Example 2 (Comparative example)

A mixture of silver(I) oxide and PTFE in the weight ratio 9:1 was milled by means of a high-speed beater mill, from IKA, type M20, at intervals of in each case 15 seconds with cooling. This mixture was rolled on a roll mill from Wetzels, comprising 2 roll shells having a width of 40 cm and a diameter of 13 cm with a roll nip of 0.18 mm over a width of 20 cm at a clamping force of 18 kN/cm. The circumferential speed was 1.35 m/min and the roughness of the roll surfaces had a Ra number of 25-30 μm . The temperature during the rolling process was 22°C. The sheet-like structure obtained had a thickness of 0.19 mm and was mechanically stable. The sheet-like structure could be applied without problems to a mechanical support, a nickel net, having a wire thickness of 0.14 mm and a mesh size of 0.5 mm. The voltage of the electrolysis cell was 2.45 V at a current density of 4 kA/m². This voltage is substantially too high for technical applications.

Example 3

A mixture of silver(I) oxide and PTFE in the weight ratio 9:1 was milled by means of a high-speed beater mill, from IKA, type M20, at intervals of in each case 15 seconds with cooling. This mixture was rolled on a roll mill from Wetzels, comprising 2 roll shells having a width of 20 cm and a diameter of 10.8 cm with a roll nip of 0.13 mm over a width of 20 cm at a clamping force of 1.0 kN/cm. The circumferential speed was 1.35 m/min and the roughness of the roll surfaces had a Ra number of 25-30 μm .

The temperature during the rolling process was 22°C. The sheet-like structure obtained had a thickness of 0.35 mm and was mechanically stable. The sheet-like structure could be applied without problems to a mechanical support, a nickel net, having a wire thickness of 0.14 mm and a mesh size of 0.5 mm. The voltage of the electrolysis cell was 2.35 V at a current density of 4 kA/m².

Example 4

A mixture of silver(I) oxide and PTFE in the weight ratio 9:1 was milled by means of a high-speed beater mill, from IKA, type M20, at intervals of in each case 15 seconds with cooling. This mixture was rolled on a self-designed roll mill, comprising 2 roll shells having a width of 40 cm and a diameter of 10.8 cm with a roll nip of 0 mm over a width of 15 cm at a clamping force of 0.5 kN/cm. The circumferential speed was 1.35 m/min and the roughness of the roll surfaces had a Ra number of 25-30 µm. The temperature during the rolling process was 22°C. The sheet-like structure obtained had a thickness of 0.35 mm and was mechanically stable. The sheet-like structure could be applied without problems to a mechanical support, a nickel net, having a wire thickness of 0.14 mm and a mesh size of 0.5 mm. The voltage of the electrolysis cell was 2.15 V at a current density of 4 kA/m².

Example 5

A mixture of silver(I) oxide and PTFE in the weight ratio 9:1 was milled by means of a high-speed beater mill, from IKA, type M20, at intervals of in each case 15 seconds with cooling. This mixture was rolled on a roll mill from Wetzol, comprising 2 roll shells having a width of 40 cm and a diameter of 10.8 cm at a roll nip of 0 mm and a clamping force of 0.5 kN/cm over a width of 30 cm. The circumferential speed was 1.35 m/min and the roughness of the roll surfaces had a Ra number of 25-30 µm. The temperature during the rolling process was 22°C. The sheet-like structure obtained had a thickness of 0.42 mm and was mechanically stable. The sheet-like structure was rolled on said roll mill onto a nickel net having a mesh size of 0.5 mm and a wire thickness of 0.14 mm so that the resulting nip force was 1 kN/cm. The circumferential speed was 1.3 m/min. The voltage of the electrolysis cell was 2.28 V at a current density of 4 kA/m².

Patent claims

1. A method for producing gas diffusion electrodes, in particular for use in electrolysis cells, in which first a sheet-like structure is produced by means of a pair of rolls by rolling a powder mixture containing at least one catalyst or a catalyst mixture and a binder and then the sheet-like structure is connected to an electrically conductive catalyst support by rolling by means of a pair of rolls, characterized in that the clamping force of the rolls is kept constant in the range from 0.2 kN/cm to 15 kN/cm.
2. A method for producing gas diffusion electrodes, in particular for use in electrolysis cells, in which first a sheet-like structure is produced by means of a pair of rolls by rolling a powder mixture containing at least one catalyst or a catalyst mixture and a binder and then the sheet-like structure is connected to an electrically conductive catalyst support by rolling by means of a pair of rolls, in particular as claimed in claim 1, characterized in that the diameter of the rolls, independently of one another, is not less than 8 cm and not more than 15 cm.
3. A method for producing gas diffusion electrodes, in particular for use in electrolysis cells, in which first a sheet-like structure is produced by means of a pair of rolls by rolling a powder mixture containing at least one catalyst or a catalyst mixture and a binder and then the sheet-like structure is connected to an electrically conductive catalyst support by rolling by means of a pair of rolls, in particular as claimed in claim 1 or 2, the sheet-like structure being applied to the catalyst support by rolling, characterized in that the rolling is effected under a nip force of from 0.1 kN/cm to 2 kN/cm.
4. The method as claimed in any of claims 1 - 3, characterized in that the clamping force of the rolls during rolling of the powder mixture is in the range from 0.2 kN/cm to 10 kN/cm, preferably from 0.2 kN/cm to 5 kN/cm, particularly preferably from 0.2 kN/cm to 2 kN/cm.
5. The method as claimed in any of claims 1 - 4, characterized in that the diameter of the rolls, independently of one another, is not less than 8 cm and not more than 13 cm, in particular not more than 11 cm.

6. The method as claimed in any of claims 1 - 5, characterized in that the circumferential speed of the rolls during rolling of the powder mixture, independently of one another, is from 0.05 m/min to 19 m/min, preferably from 0.1 m/min to 15 m/min.
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7. The method as claimed in any of claims 1 - 6, characterized in that the circumferential speed of the rolls during connection of the sheet-like structure to the support, independently of one another, is from 0.1 m/min to 12 m/min, preferably from 0.8 m/min to 2 m/min.
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8. The method as claimed in any of claims 1 - 7, characterized in that the sheet-like structure has a thickness of from 0.05 mm to 0.7 mm, preferably from 0.15 mm to 0.6 mm.
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9. The method as claimed in any of claims 1 - 8, characterized in that the temperature of the sheet-like structure and/or of the catalyst support during the rolling processes is from 5°C to 70°C.
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10. The method as claimed in any of claims 1 - 9, characterized in that the rolls, independently of one another, have a surface roughness of from 0.05 μm to 1.5 μm .
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11. The method as claimed in any of claims 1 - 10, characterized in that the electrically conductive catalyst support is connected to a gas-permeable, metallic baseplate.