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(54) Benævnelse: FREM GANGSMÅDE TIL FREMSTILLING AF EN DIAMANTELEKTRODE

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The invention concerns a method of producing a diamond electrode with synthetically produced and electrically conductive (doped) diamond particles which are embedded in a carrier layer of electrically non-conductive material.

Diamond electrodes are characterised in having an increased overpotential for oxygen and hydrogen and are therefore especially suitable for a large number of oxidation processes in aqueous solution. Particularly interesting applications may be found in the field of water treatment using anodic oxidation, as well as in synthetic chemistry.

It is known that diamond electrodes can be produced by creating diamond layers doped with boron right on to substrate materials, in particular by the CVD (chemical vapour deposition) method, as disclosed, for example, in DE 10324558. A method of producing diamond electrodes is known from EP 1527212 in which doped, electrically conductive and synthetically produced diamond particles are embedded superficially in a metal or a metal alloy such that a conductive connection is made between the metal or metal alloy and the diamond particles. The diamond particles are mixed and then pressed with powders of metals or metal alloys which are able to form a non-conductive oxide layer so that a pressed part, possible with a carrier plate, is formed which contains the diamond particles embedded in one or more layers. The basic materials recommended for use as the embedding layer are low melting point materials such as magnesium or a magnesium alloy which are fused on to a preferably metallic carrier layer with a high melting point.

With regard to the prior art, reference is made to WO 2005116298 which concerns the production of synthetic diamond electrodes, to JP 2005272908 from which a bipolar diamond electrode is known, and to US 2005200260 which discloses a method in which metal is deposited on diamonds.

Diamond electrodes produced by the cited CVD method are limited as regards their size. Because of the difference in the thermal expansion coefficients, larger electrode surfaces have a tendency to crack which can lead to the subsequent breakdown of the electrode due to the formation of gas under the diamond layer. Therefore, in order to ensure the stability of the electrode, the diamond layer must have a minimum thickness which can only be achieved by a depositing process lasting several hours. Thus, the production costs are comparatively high when diamond electrodes are produced by this method.

Diamond electrodes produced according to EP 1527212 by attaching diamond particles to self-passivating metals are very stable in those media in which the metal oxide is stable under anodic or cathodic conditions. In highly halogenide-containing aqueous solutions and in organic solutions as used in electro-organic synthesis, the stability of these types of electrodes is somewhat lower. Hydride corrosion impairs the stability of the electrodes in alternating current applications.

The invention is based on the task of providing a method of producing highly stable diamond electrodes
in aggressive media and equivalent diamond electrodes. Diamond electrodes produced according to the invention are intended to be particularly stable in halogen acids, in salt solutions, brine, sea water and in organic synthesis with alcoholates.

The assigned task is resolved inventively by firmly attaching two carrier layer-forming films to each other between which the doped diamond particles are embedded in single layers wherein the diamond particles are then exposed to both sides of the carrier layer.

Diamond electrodes produced and made according to the invention can be produced so that they are very stable by the choice of the film material in the cited aggressive media, such as halogen acids, salt solutions, brine, and sea water and in organic synthesis with alcoholates. They can be used across the entire pH range from 0 to 14. Furthermore, diamond electrodes according to the invention are largely maintenance-free since deposits such as calcium oxide can be dissolved by reversing the polarity, avoiding the need for acid washing. Diamond electrodes produced and made according to the invention can also be used as anodes or as cathodes in which their polarities can be reversed frequently or they can be operated with an alternating current without the electrodes being damaged by hydride formation.

According to a preferred embodiment of the invention, glass, ceramic or a plastic, in particular PVDF, PFA, PTFE, FEP, ETFE, PEEK or PPS can be used as the material for the carrier layer to mechanically attach the diamond particles, (claim 2). These materials are well suited under cathodic and anodic conditions in equal measure and are not sensitive to hydride corrosion, oxygen corrosion or other chemical effects.

In a preferred alternative embodiment of the invention, the films between which the doped diamond particles are placed have a thickness of 5 µm to 300 µm, preferably 10 µm to 150 µm (claim 6).

Heating (above the melting temperature), welding, soldering, sintering, pressing, rolling or gluing, for example, are suitable for attaching the two films to each other (claim 2).

In a preferred embodiment of the invention, to increase the mechanical strength, a supporting web, supporting tissue or similar is inserted between the two films before they are joined together. In an alternative embodiment, the web or tissue can be fixed on one or both sides to the surface of the diamond electrode also after producing the diamond electrode by common methods involving plastic to plastic, or plastic to metal attachments, such as by laminating or gluing (claim 7). Plastics such as PVDF, PFA, PTFE, FEP, ETFE, PEEK or PPS, glass fibres, plastic-coated glass fibres, ceramics or metals such as titanium or tantalum are used as materials for the supporting tissue or supporting web (claim 8).

In a preferred manner, the diamond particles are exposed already in the heating operation (melting). In order to expose the diamond particles on both sides, an additional soft material in the form of thin plates
is placed on the outer side of the carrier layer-forming films into which the diamond particles are pressed by applying pressure on one or both sides, thereby exposing them. Polytetrafluoroethylene, polyimide, neoprene (polychloroprene), thermoplastic vulcanisates (TPV), fluropolymerisates, fluorocarbon elastomers such as FPM or FKM, PEEK, silicone or also metals such as lead, aluminium or copper are examples of materials that can be considered to use for these plates (claim 3). In this case, the thickness of these materials is 0.2 mm to 3 mm, or in a preferred embodiments 0.5 mm to 1.5 mm (claim 4).

Alternatively or, if required, in a further operation the diamond particles are exposed on both sides of the carrier layer in a mechanical, chemical or thermal manner (claim 5). By doing this, under any circumstances contact can be guaranteed to be made with the diamond particles on both sides of the carrier layer.

A contacting layer can be attached to the blank thus produced on one side which ensures that the diamond particles can be supplied with current at all times. Mainly graphite, carbon or carbon fibres are possible as the electrically conducting material. This material can take the form of a powder, paste or a tissue (claim 9).

A conducting salt solution, preferably Na₂SO₄, can be used in the contacting layer to improve the contact.

The invention is explained in more detail with the aid of the drawing which illustrates one embodiment. The one drawing, Fig. 1, shows diagrammatically a cross section through a diamond electrode designed and made according to the invention.

The diamond electrode shown in the drawing consists of a layer of diamond particles 2 which are embedded in a carrier layer 1. The diamond particles 2 are embedded in single layers in the carrier layer 1 without being in mutual contact with each other such that they project somewhat on both sides out of the carrier layer 1 and are exposed. A contacting layer 3 of an electrically conducting material is attached on the one side of the carrier layer 1. The current 4 is supplied through the contacting layer 3.

Diamond particles 2 differing on shape and size and from different manufacturing processes can be used for diamond electrodes according to the invention. Conducting or semi-conducting diamond powder with a grain size of 80 μm to 500 μm, in particular up to 300 μm is especially suitable. The diamond particles 2 are doped in particular with boron or nitrogen. Boron-doped industrial diamonds produced in a high pressure, high temperature process and having an especially high proportion of sp3 carbon are a preferred basic material for the production of diamond electrodes according to the invention.

The carrier layer 1 serves to fix the diamond particles 2 mechanically, particularly in one plane, and consists of an inert material in an appropriate application medium under cathodic and anodic conditions, and which is preferably insensitive to hydride corrosion, oxygen corrosion and other chemical effects.
Glass, ceramic and chemically stable polymers such as fluorinated polymers such as polytetrafluoroethylene, PVDF, PFA, PTFE, FEP, ETFE, PEEK or PPS are especially suitable.

Films constitute the basic material for the carrier layer 1. When films are used, the diamond particles 2 are embedded between two films of the selected material, such as glass, ceramic or plastic. Then, the two films are attached to each other, for example, by heating (fusion), welding, soldering, sintering, pressing, rolling or gluing. The thickness of the films is 5 µm to 300 µm, preferably from 10 µm to 150 µm. The raised parts of the diamond particles are exposed on both sides, such as in a mechanical, chemical or thermal manner.

It is especially advantageous if the diamond particles have been exposed already when heating or melting both films on the outer sides of the films. For this purpose, a soft material in the form of thin plates is attached respectively on the films forming the carrier layer. By applying surface pressure to one or both sides, the diamond particles penetrate through the film material and are exposed as a result. Polytetrafluoroethylene, a fluoropolymer elastomer, polyimide, neoprene, thermoplastic vulcanisates (TPV), fluoropolymerisates such as PO, fluorocarbon elastomers such as FPM or FKM, PEEK, silicones or also metals such as lead, aluminium or copper are examples of materials that can be considered as preferred materials to use for the thin plates. The thickness selected for the plates is between 0.2 mm to 3 mm, in particular between 0.5 mm and 1.5 mm. If necessary, a further operation can be carried out in a mechanical, chemical or thermal manner to completely expose the diamond particles.

To increase the mechanical strength of the diamond electrode, in producing the diamond electrode a supporting web, supporting tissue or similar is inserted between the two films. However, it is also possible to fix a supporting web, supporting tissue or similar on one or both outer sides after producing the diamond electrode.

In order to do this, the common methods of joining metals or plastics can be considered, such as laminating or gluing. Plastics such as PVDF, PFA, PTFE, FEP, ETFE, PEEK or PPS, glass fibres, plastic-coated glass fibres, ceramics or metals such as titanium or tantalum are suitable for use as materials for the supporting tissue or supporting web.

A contacting layer 3 can be attached to one side of the carrier layer 1, enabling the diamond particles 2 to have a constant current supply. In principle, all types of conducting materials are suitable for the contacting layer 3. However, it should be borne in mind that it is hardly possible to have a sustainable and leak-tight attachment of the diamond particles 2 in the carrier layer 1. It is not out of the question that, as the electrode is operating, the diamond particles 2 become detached from the carrier layer 1 in some places. The processes that may cause a detachment in this event are not only chemical in nature, such as by oxidation or corrosion, but the causes might be physical also. For instance, a build-up of heat
through the flow of current can result in the formation of cracks between the diamond particles 2 and the carrier layer material. Also, the formation of gases at the anodically or cathodically operated diamond electrode can give rise to strong forces which have the effect of slowly weakening the attachment. While the diamond particles 2 may still be in their position after a certain operating period, it is nevertheless possible for liquid to penetrate the contacting layer 3.

In order to ensure stability over the long term in aggressive media also, it is important to design the contacting layer 3 such that, despite the penetration of liquid and the possible corrosion of the material of the contacting layer 3, permanent contact with the diamond particles 2 is guaranteed. Applications exposing the diamond electrode to halogen salts, halogen acids and alcohoholates under anodic conditions eliminate practically all metallic conductors as a material for the contacting layer 3. According to the invention therefore, either conducting materials such as ceramics or plastics, or materials such as graphite, carbon or carbon fibres are used for the contacting layer 3.

Conducting forms of carbon, such as graphite, carbon or carbon fibres 3 are highly suitable for the contacting layer. While these materials oxidise in contact with the solution under an anodic potential, they do not form carbon dioxide which escapes through the material which is porous since it is present as a filler consisting of particles, powder, paste or tissue. The material backfills and provides a permanent contact with the diamond particles. A certain loss of carbon has to be accepted which is compensated for by an appropriate reserve supply of the material of the contacting layer. The total amount of current used just in the contacting (electrolysis) is negligible in comparison to that supplied by the diamond particles 2.

In order to avoid excessive electrolysis at the contacting layer 3, the contacting layer 3 can be drained whereby any penetrating solution on the contacting layer 3 can be actively removed. This is done through suitable openings 4 preferably by means of the gas pressure arising from the electrolysis in the contact space.

In order to make the contact, the contacting layer 3 can be filled additionally with a conducting salt solution, preferably a Na₂SO₄ solution, or can consist of carbon powder mixed with concentrated Na₂SO₄.

In order to ensure that the contacting layer material backfills to the electrode, it is advantageous to press the contacting layer 3 against the carrier layer 1 at a constant pressure. This can be done in different ways, such as by applying a force to a rear wall, by devices with springs, by hydraulic devices and similar methods. Another possibility involves the use of the gas pressure from the electrolysis in the contact space.

Diamond electrodes produced and made according to the invention can also be used as bipolar electrodes incorporated in an electrochemical cell. Electrochemical cells of this type are used in a variety of
applications, such as the treatment of water and effluent in industrial operations, to purify water in swimming baths or whirlpools, and to disinfect drinking water.
Patentkrav

1. Fremgangsmåde til fremstilling af en diamantelektrode med syntetisk fremstillede og elektrisk ledende (doterede) diamantpartikler (2), der er indlejret i et bærelag (1) af et elektrisk ikke-ledende materiale, kendetegnet ved, at to bærelagsdannende film, hvor imellem de doterede diamantpartikler (2) er indlejret i enkelte lag, er fast forbundet med hinanden, hvor diamantpartiklerne derefter eksponeres på begge sider af bærelaget (1).

2. Fremgangsmåde ifølge krav 1, kendetegnet ved, at filmene består af glas, keramik eller plast, såsom PVDF, PFA, PTFE, FEP, ETFE, PEEK eller PPS, og forbindes med hinanden ved opvarmning, svejsning, lodning, sintring, presning, valsning eller limning.

3. Fremgangsmåde ifølge krav 1 eller 2, kendetegnet ved, at, der for at eksponere diamantpartiklerne på filmene anbringes bløde materialer i form af plader på dem og påføres et tryk på én eller begge sider, hvor pladerne fortrinsvis består af polytetrafluorethylen, polyimid, polychlorpropen, termoplastiske vulkanisater (TPV), fluorphomerisater, fluorcarbonelastomerer, såsom FPM eller FKM, PEEK, silikoner eller bløde metaller, såsom bly, aluminium eller kobber.

4. Fremgangsmåde ifølge krav 3, kendetegnet ved, at pladernes tykkelse er fra 0,1 mm til 3 mm, navnlig fra 0,5 mm til 1,5 mm.

5. Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 4, kendetegnet ved, at diamantpartiklerne (2) er eksponerede på begge sider af bærelaget (1) på en mekanisk, kemisk eller termisk måde.

6. Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 5, kendetegnet ved, at filmenes tykkelse er fra 5 μm til 300 μm, fortrinsvis fra 10 μm til 150 μm.

7. Fremgangsmåde ifølge et hvilket som helst af kravene 1 til 6, kendetegnet ved, at et støttevæv eller et støtegitter er indsat enten mellem de to film, inden de forbindes med hinanden, eller er fastgjort på én eller begge ydre sider af bærelaget/bærelagene eller diamantelektroden, hvor støttevævet eller støtegitteret er fastgjort, navnlig ved laminering, limning, smeltning, svejsning, presning eller valsning.

8. Fremgangsmåde ifølge krav 7, kendetegnet ved, at plast, såsom polytetrafluorethylen, PVDF, PFA, PTFE, FEP, ETFE, PEEK eller PPS, eller også glas fibre, plastcoatede glas fibre, keramik
eller metaller, såsom titan eller tantal, anvendes som materiale til støttevævet eller støtregitteret.

9. Fremgangsmåde ifølge krav 1, kendtegnet ved, at der for etablering af kontakt mellem diamantpartiklerne (2), på én side af bærelaget (1), er fastgjort et kontaktlag (3) af et elektrisk ledende materiale, navnlig grafit, carbon eller carbonfibre, der hverken danner isolerende oxid eller går i opløsning under de særlige forhold, hvorunder diamantelektroden anvendes.