A process for producing a coated, structured heat exchanger plate for a reactor in a fuel cell system comprises application of a catalytic component in at least one layer by means of pad printing, exclusively in the recesses and/or the flanks of the heat exchanger plate.
CATALYTIC COATING OF STRUCTURED HEAT EXCHANGER PLATES

[0001] This application claims the priority of German Patent Document DE 101 29 099.3, filed Jun. 16, 2001, the disclosure of which is expressly incorporated by reference herein.

BACKGROUND AND SUMMARY OF THE INVENTION

[0002] The invention relates to a process for producing a coated, structured heat exchanger plate for a reactor in a fuel cell system.

[0003] A process for applying electrode layers to a strip form polymer electrolyte membrane for fuel cells is described in DE 199 10 773 A1. The electrode layers are continuously printed in the desired pattern on the front and rear surfaces of the membrane using an ink which contains an electrocatalyst. The electrode layers which have been printed on the membrane are dried at elevated temperature immediately after the printing operation. The printing is carried out so as to maintain a positionally accurate arrangement of the patterns of the electrode layers on front and rear surfaces. The printing operation in this case is carried out on a planar surface. In addition, the printing may be accomplished by stencil printing, offset printing or screen printing, or be carried out by means of pad printing.

[0004] Hitherto, structured heat exchanger plates have usually been spray-coated, wash-coated or dip-coated in order for coatings to be applied. However, spray-coating causes a loss of coating material of up to 50% as a result of overspray. During the production of welded, structured heat exchangers comprising spray-coated plates which are coated over their entire surface, layer flaking occurs at the contact points. If welded reactors of this type are wash-coated or dip-coated, deposits form at the contact points and these deposits likewise flake off readily when thermal stresses occur. The resulting drawback in the form of discharged catalyst dust leads not only to higher costs on account of the loss of catalyst but also to disruptions to the entire fuel cell system. The disruptions occur through the presence of impurities in the pipeline systems which results in, inter alia, the filters becoming blocked, ignition in undesirable areas of the system, and damage to valves.

[0005] Therefore, it is an object of the invention to provide an inexpensive process for coating a structured heat exchanger plate for a reactor, in which discharge of catalyst as a result of mechanical and/or thermal stress during production or when a fuel cell system is operating is virtually avoided.

[0006] To achieve this object, the present invention provides a process for producing a coated, structured heat exchanger plate for a reactor in a fuel cell system in which a catalytic component is applied continuously or discontinuously in at least one layer, by means of pad printing, exclusively in the recesses and the flanks of the heat exchanger plate.

[0007] Further advantages of the process according to the invention result from the high reliability of the process and the resulting high-quality product, and the fact that process steps are eliminated. Moreover, this process is far more environmentally friendly than the other processes mentioned, since this process does not cause any spray mist or overspray which has to be discharged and disposed of.

[0008] The invention is illustrated diagrammatically and by way of example in the drawings and is explained in more detail below with reference to the drawings.

BRIEF DESCRIPTION OF THE INVENTION

[0009] FIG. 1 shows a plan view of a corrugated plate;

[0010] FIG. 2 shows the overlap of the corrugations when the plates are stacked and resulting contact points;

[0011] FIG. 3 shows a cross section through two welded, corrugated plates; and

[0012] FIG. 4 shows an outline sketch for the pad printing of a corrugated plate.

DETAILED DESCRIPTION OF THE INVENTION

[0013] In the process according to the invention for the production of a coated, structured heat exchanger plate 1 for a reactor in a fuel cell system, a catalytic component is applied continuously or discontinuously in at least one layer, by means of pad printing, exclusively in the recesses 2 and/or flanks 3 of the heat exchanger plate 1. (See FIG. 4.) Therefore, no coating is applied to the surface of the raised parts 4 of the heat exchanger plate. When the individual heat exchanger plates are joined to form reactors, which are only peripherally welded, therefore, the contact surfaces 5 or contact points are not covered with the catalytic component. This targeted coating minimizes the release or flaking of the catalyst that leads to catalyst being discharged as a result of mechanical and/or thermal stress.

[0014] The coating of these structured plates is carried out by means of pad printing. Pad printing is an indirect printing process, i.e. a plate, which is known as an engraving, serves as the original, on which the image to be printed is present in the form of a recess. What is known as a printing paste or printing liquid is spread over the engraving by means of a doctor blade and is then drawn off again. The printing paste or printing liquid remains in place in the recesses in the engraving. A smooth, elastic stamp, known as the pad 6, preferably produced from silicone rubber, being pressed on, picks up some of this coating material from the recesses and transfers this material to the object 1 which is to be coated. The elasticity of the silicone rubber means that the pad 6, as illustrated in FIG. 4, can match the object which is to be printed when it is releasing the printing paste or printing liquid. This allows the printing of non-planar, structured plates, in which advantageously only the recesses 2 and/or flanks 3 but not the raised surfaces 4 of the structured plate 1 are to be printed.

[0015] The coating of the heat exchanger plate with the catalytic component can take place by one or more imprints covering the entire area of the plate. However, the coating may also be effected by coating the heat exchanger plates in zones. Multiple printing allows the individual layers to be functionalized, so that, for example, a different catalyst is applied to the reactor inlet from that applied to the reactor outlet. Alternatively, or in addition, the quantity of catalyst can be varied over the length of the plate, in order to set up...
a gradient. In both the above cases, this procedure is used to selectively control conversions and reactions within the reactor.

[0016] If it were desired to carry out this procedure by means of spray-coating, complex masking of the respective zones would be necessary. This would make the process unnecessarily expensive and relatively complex to realize, in addition to the overspray effect. Zoned coating cannot be achieved by means of wash-coating or dip-coating, so at best it is possible to apply a gradient in coating height using these methods. The above process can be carried out either discontinuously or continuously, with the plate or plate strip being stopped briefly during the printing operation, printed and then moved onward by a defined repetition length under the control of sensors. The layer thicknesses applied by means of pad printing are in the range of approximately 5 to 50 µm of total layer thickness.

[0017] The catalytic component which is to be applied by pad printing contains a catalytically active material component and/or a hydrophobic material component. The coating with the respective material components may take place in mixed form or as individual layers. For example, a lower layer, which contains the catalytically active material component, can be printed onto the plate, followed by an upper layer, which contains the hydrophobic material component, printed onto the lower layer. Since the pad printing can be applied not only in the form of a complete area but also in the form of patterns, a first application of the catalytically active material component, can be accomplished where it is not covered completely by the subsequent printing of the hydrophobic material component. This ensures that the reaction gases and/or vapors can still reach the catalyst, and therefore the catalytic activity is retained but “flooding of the catalyst”, i.e. complete coverage of the catalyst with droplets and/or a film of liquid through condensation of water vapor, with the associated reduction in activity or deactivation of the catalyst, is avoided. Therefore, the combination of the catalytically active material component with the hydrophobic material component ensures that the reactivity of the catalyst is not impaired by the formation of condensate at cool points of the fuel cell system, but rather is as far as possible available in particular during a cold start. At the same time, this combination, through adhesive bonding and/or crosslinking, advantageously prevents the catalyst from flaking off or being discharged or reduces these effects as far as possible.

[0018] As has already been described in the patent application DE 10114646.9 in the name of the Applicant, which is not a prior publication, the catalytically active material selected is preferably metals from subgroups IIb, IIIb, VIb and/or Vllb of the periodic table; substances which are based on elements from other groups of the periodic table, such as oxides of the rare earths, may also be present in order to thermally stabilize the catalyst. The at least one catalytic material component and/or catalyst-containing material component is preferably in supported form. There is a wide range of support materials for catalysts, such as ceramic, carbon, plastic and metal. Porous solids, on the surface of which catalytically active material is deposited, are particularly suitable. Ceramic materials, such as zeolites, Al₂O₃, SiO₂, ZrO₂, CeO₂ and/or mixtures thereof, are particularly preferred for use as support materials.

[0019] The at least one hydrophobic material preferably contains silicones or silicone-containing materials, fluorinated polymers, such as for example polytetrafluoroethylene or perfluoralkoxyethylene-containing materials, epoxy resin or epoxy-resin-containing materials, phenolic resin or phenolic resin-containing materials, acrylic resin or acrylic resin-containing materials, PUR adhesive materials or PUR adhesive-containing materials or synthetic resin/shellac mixtures or synthetic resin-containing/shellac-containing mixtures. In the field of the fluorinated polymers, polytetrafluoroethylene (PTFE) is a particularly suitable hydrophobic component and binder for catalysts. With regard to the silicones, it is particularly preferred to use silicone resins, which must have a high long-term thermal stability in the range of use. These use temperatures lie in the range between approximately 30°C to 650°C, preferably in the range between approximately 50°C to 300°C. A further advantage comes from the fact that, when precious metal is used as the catalytically active material component in combination with silicones as the hydrophobic material component, there are no poisoning phenomena caused by catalyst poisons, as is the case, for example, when copper is used as catalytic component.

[0020] Moreover, it is extremely advantageous if the layer which contains the hydrophobic material component has an elasticity which results from the chemical substance itself and additionally prevents flaking or discharge of the catalyst from the layer or substantially reduces these effects. The crosslinking of the hydrophobic material component leads to the latter acting as a binder for the catalyst. The proportion of hydrophobic material component in relation to the catalytically active material component and/or catalyst-containing material component is 1 to 50% by weight, preferably 5 to 25% by weight.

[0021] The catalyst paste or suspension or liquid which is required for printing may preferably include, in addition to at least one catalytically active material component, a ceramic binder, which can also be crosslinked after calcining in air at approximately 500°C, and water. Oxides and/or hydroxides of Al, Ce, Si, Zr and/or mixtures thereof, are suitable ceramic binders; it is preferable to use those which can be crosslinked.

[0022] If the catalyst paste or suspension or liquid which is required for printing contains a polymeric binder which decomposes at the temperatures required for calcining, the calcining step is eliminated and all that follows is one or more drying steps. One exception to this is the use of PTFE as polymeric binder, since this material is able to withstand relatively high temperatures for a short time.

[0023] Further additives, for example for controlling the viscosity, the wetting behavior on the stamp or to set the pH, may also be present in the printing paste, suspension or liquid. To achieve an optimum printed image, the shape of the stamp must be matched to the area which is to be printed. The matching of the process parameters to the printing operation are dependent on the material, temperature and process step and can be achieved by means of standard specialist printing knowledge.

[0024] The printing operation itself is preferably carried out at room temperature, without the printing medium (the stamp or pad) or the coating material (printing paste, suspension or liquid) being heated.
During the application of the catalytic component, the heat exchanger plate can be heated to up to 200°C. This advantageously results in more rapid drying of the coating material, particularly during multiple printing.

If the heat exchanger plate is not heated when the printing paste, suspension or liquid is being applied to it, the printing step is followed by a drying step in a temperature range from approximately 100°C to 200°C in order to improve adhesion of the coating. Circulating-air/continuous dryers, but also radiation dryers, for example those using infrared, can be used for drying. The drying time required is governed by the rate of passage of the plate or plate strip. Further printing operations may follow the drying step.

Then, the calcining step which concludes the process is carried out at approximately 500°C, contributing to final drying and to crosslinking of the ceramic binder contained in the coating. The duration of the calcining step is between 0.5 and 4 hours.

If, for example, silicone or silicone-containing material, which decomposes at the temperatures required for calcining, is used as hydrophobic material component, the calcining step has to take place before the application of the silicone or silicone-containing material. To dry the silicone or silicone-containing layer which is subsequently applied, one or more drying steps are subsequently carried out.

The heat exchanger plates which are produced using the process according to the invention are equally suitable for use as reactor in hydrogen, reformate and direct methanol fuel cell systems.

The foregoing disclosure has been set forth merely to illustrate the invention and is not intended to be limiting. Since modifications of the disclosed embodiments incorporating the spirit and substance of the invention may occur to persons skilled in the art, the invention should be construed to include everything within the scope of the appended claims and equivalents thereof.

What is claimed is:

1. A process for producing a coated, structured heat exchanger plate for a reactor in a fuel cell system, comprising: applying a catalytic component continuously or discontinuously in at least one layer, by means of pad printing, exclusively to at least one of recesses and flanks of the heat exchanger plate.

2. The process according to claim 1, wherein:
   said catalytic component is applied in at least two stages; and
   each stage is in a different zone of the heat exchanger plate.

3. The process according to claim 1, wherein said catalytic component contains at least one of a catalytically active material component and a hydrophobic material component.

4. The process according to claim 3, wherein said catalytically active material component is in supported form.

5. The process according to claim 3, wherein said catalytically active material component contains at least one of a ceramic binder and a polymeric binder.

6. The process according to claim 3, wherein at least one of composition and concentration of said catalytically active material component is varied over the length of the heat exchanger plate.

7. The process according to claim 1, wherein:
   the process is carried out at room temperature; and
   the printing medium and coating material are not heated.

8. The process according to claim 7, further comprising a drying step at a temperature between 100°C to 200°C, inclusive, subsequent to said applying by means of pad printing.

9. The process according to claim 7, wherein the heat exchanger plate is heated while the catalytic component is being applied.

10. The process according to claim 8, further comprising a final step of calcining at a temperature of approximately 500°C.

11. A process for producing a coated, structured heat exchanger plate for a fuel cell reactor, comprising:
   applying at least one layer of a catalytic component to at least one region of the heat exchanger plate with a printing medium,
   wherein said catalytic component is applied exclusively to at least one location selected from the group consisting of: the heat exchanger plate recesses and the heat exchanger plate flanks.

12. The process according to claim 11, wherein said at least one layer comprises at least two different catalysts.

13. The process according to claim 11, wherein said at least one layer comprises a thickness of 5 to 50 μm.

14. The process according to claim 11, wherein a gradient is created by applying said catalytic component in at least two different thicknesses.

15. The process according to claim 11, wherein said catalytic component is a catalytically active material.

16. The process according to claim 15, wherein said catalytically active material further comprises a thermal stabilizing agent.

17. The process according to claim 11, wherein said catalytic component is a hydrophobic material.

18. The process according to claim 11, wherein said catalytic component is a combination of a catalytically active material and a hydrophobic material.

19. A device for coating a heat exchanger plate for a fuel cell reactor, said heat exchanger having a three dimensional structured contour including a plurality of recesses and flanks, said device comprising:
   said printing pad,
   wherein said printing pad is made of a smooth elastic material which is deformable to match the three dimensional contour of the heat exchanger plate by being pressed thereon;
   whereby a catalytic component applied on said printing pad is deposited in the form of at least one layer on at least one of the flanks and recesses of said three dimensional contour.

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