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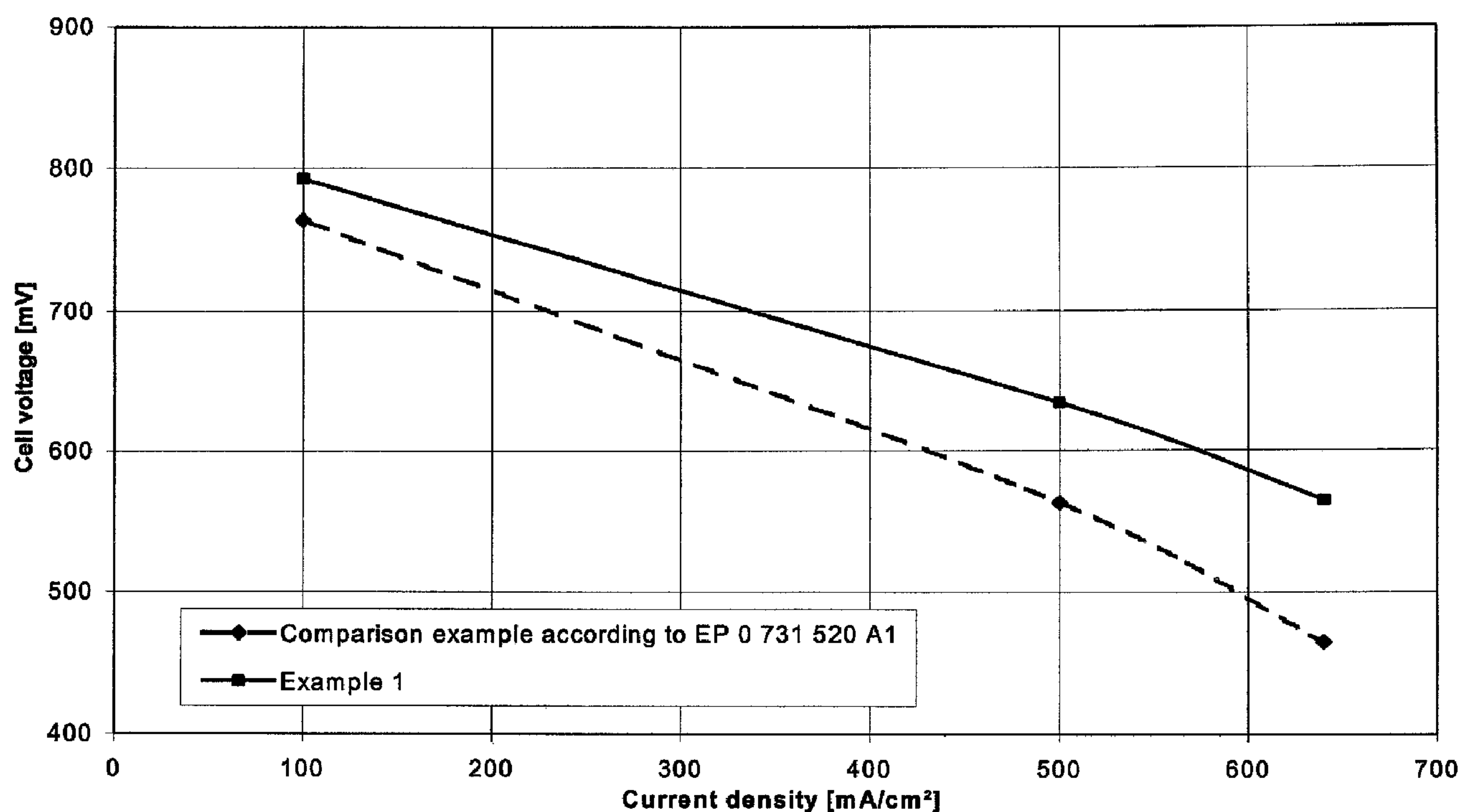
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(54) Title: AN INK FOR PRODUCING MEMBRANE ELECTRODE UNITS FOR PEM FUEL CELLS



(57) Abrégé/Abstract:

The invention provides an ink for producing membrane electrode units for PEM fuel cells which contains a catalyst material, an ionomer, water and an organic solvent. The ink is characterised in that the organic solvent is at least one compound from the group of linear dialcohols with a flash point higher than 100°C and is present in the ink in a concentration between 1 and 50 wt.%, with respect to the weight of water.

990226 KY IP**Abstract**

The invention provides an ink for producing membrane electrode units for PEM fuel cells which contains a catalyst material, an ionomer, water and an organic solvent. The ink is characterised in that the organic solvent is at least one compound from the group of linear dialcohols with a flash point higher than 100°C and is present in the ink in a concentration between 1 and 50 wt.%, with respect to the weight of water.

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**An ink for producing membrane electrode units
for PEM fuel cells**

Description

5 The present invention provides an ink for producing membrane electrode units for fuel cells, in particular for polymer electrolyte membrane fuel cells (PEM fuel cells). A novel type of water-based catalyst ink for producing membranes coated with catalyst, electrodes and membrane electrode units (MEUs) is described.

10 Fuel cells convert a fuel and an oxidising agent which are spatially separated from each other at two electrodes into electricity, heat and water. Hydrogen or a hydrogen-rich gas may be used as the fuel and oxygen or air as the oxidising agent. The process of energy conversion in the fuel cell is characterised by particularly high efficiency. For this reason, fuel cells in combination with electric motors are becoming more and more important as an alternative to traditional internal combustion engines. The PEM fuel cell is suitable for use as an energy converter in motor vehicles because of its compact
15 structure, its power density and its high efficiency.

The PEM fuel cell consists of a stacked arrangement ("stack") of membrane electrode units (MEUs), between which are arranged bipolar plates for supplying gas and removing electricity. A membrane electrode unit consists of a solid polymer electrolyte membrane, both faces of which are provided with reaction layers containing catalyst.
20 One of the reaction layers is designed as an anode for the oxidation of hydrogen and the second reaction layer is designed as a cathode for the reduction of oxygen. To these reaction layers are applied so-called gas distributor layers made of carbon paper or carbon fleece which facilitate good access by the reaction gases to the electrodes and effective removal of the cell current. The anode and cathode contain so-called
25 electrocatalysts which catalytically support the particular reaction (oxidation of hydrogen at the anode or reduction of oxygen at the cathode). Metals from the platinum group in the periodic system of elements are preferably used as the catalytically active components. In the majority of cases, so-called supported catalysts, in which the catalytically active platinum group metal has been applied in highly disperse form to the
30 surface of a conductive support material, are used.

The polymer electrolyte membrane consists of proton-conducting polymer materials. These materials are also called ionomers for short in the following. A

tetrafluorethylene/fluorovinylether copolymer with acid functions, in particular sulfonic acid groups, is preferably used. Such materials are sold, for example, under the tradenames Nafion[®] (E.I. DuPont) or Flemion[®] (Asahi Glass Co.). However, other, in particular fluorine-free, ionomer materials such as sulfonated polyetherketones or arylketones or polybenzimidazoles may also be used. In addition, ceramic membranes and other high-temperature materials may also be used.

The performance data for a fuel cell depends critically on the quality of the catalyst layers applied to the polymer electrolyte membrane. These layers are mostly highly porous and usually consist of an ionomer and a finely divided electrocatalyst dispersed therein. Together with the polymer electrolyte membrane, so-called three-phase interfaces are formed in these layers, wherein the ionomer is in direct contact with the electrocatalyst and the gases (hydrogen at the anode, air at the cathode) introduced to the catalyst particles via the pore system.

To prepare the catalyst layers, ionomer, electrocatalyst, solvent and optionally other additives are carefully blended together to form an ink or a paste. To produce the catalyst layer, the ink is applied by brushing, rolling, spraying, spreading or printing either to the gas distributor structure (e.g. carbon fleece or carbon paper) or directly to the polymer membrane, dried and optionally aftertreated. In the case of coating the ionomer membrane with a catalyst layer, the non-catalysed gas distributor structures are then mounted on the membrane on the anode and cathode faces and a membrane electrode unit (MEU) is then obtained. If the gas distributor is coated with a catalyst layer, these catalysed gas distributor structures are placed on the two faces of the ionomer membrane and then compression moulded with this, wherein a MEU is also obtained.

Various ink formulations are disclosed in the patent literature. Thus, in DE 196 11 510 A1, an ink is used to produce membrane electrode units for fuel cells which contains, with respect to the total weight of ink, 3.1 wt.% of a Pt/C catalyst (30 wt.% platinum on carbon black), 30.9 wt.% of a 5% strength ionomer solution in a mixture of 90 parts isopropanol and 10 parts water, 37.2 wt.% glycerine, 24.8 wt.% water, 2.5 wt.% tetrabutylammonium hydroxide and 1.5 wt.% of a pore-producer. The water content of the ink is 27.7 wt.% in total. As a result of the high concentration of isopropanol in this ink, appropriate measures have to be taken during production to prevent unwanted ignition of the catalyst. In addition, it has been shown that the ink can be processed only over a very short time by means of a screen printing process due to the low boiling point

of isopropanol; the so-called "screen life" during which screen printing is possible is unsatisfactory. Furthermore, the glycerine present in the ink means that the membrane electrode unit (MEU) requires a very long activation and running-in period before acceptable electrical values are obtained.

5 Furthermore, catalyst inks are known which use alcohols with a boiling point higher than 100°C (US 5,871,552) or alkylene carbonates such as, for example, propylene carbonate (US 5,869,416) as solvent. Furthermore, DE 198 12 592 A1 describes an ink of two organic solvents A and B which are not miscible with each other. Monohydric or polyhydric alcohols, glycols, glycol ether alcohols, glycol ethers and mixtures thereof
10 are used as solvent A. Solvent B is a non-polar hydrocarbon or weakly polar solvent. A typical ink of this type (see example 1 in DE 198 12 592 A1) contains 13.4 wt.% of a Pt/C electrocatalyst, 67 wt.% of a 6.7% strength solution of an ionomer (Nafion) in propylene glycol (solvent A), 17.9 wt.% methyl dodecanoate (solvent B) and 1.7 wt.% of caustic soda solution (10% strength). None of these catalyst inks contain any water,
15 only organic solvents. Due to the high proportion of solvent, they tend to ignite. The considerable emissions of organic compounds (solvents are "volatile organic compounds" = VOCs) is a problem with regard to occupational health and safety and the protection of the environment, in particular when mass producing components for fuel cells.

20 Therefore inks have been disclosed in which the solvent is substantially water. Thus, EP 0309337 A1 describes a water-containing electrode ink which contains alcohols and water. The ionomer is dissolved in a mixture of water and ethanol, or isopropanol, wherein the water content is greater than 86 vol.%.

EP 0 026 979 A2 describes an ink based on water but which does not contain an
25 ionomer, rather hydrophobised Teflon™. This ink is therefore unsuitable for the electrodes and MEUs which are used in PEM fuel cells.

EP 0 731 520 A1 describes an ink which contains a catalyst, ionomer and solvent, wherein water is used as solvent. This ink does not contain any further organic components, apart from the ionomer. When the present inventor checked this ink, it was
30 shown that it led to electrode layers which adhered too poorly to the polymer membrane. As a result, the electrical performance of MEUs produced with this ink is inadequate. Likewise, when screen printing with this ink, it was shown that it thickened very rapidly and thus had inadequate screen lives for screen printing.

Thus, it was the object of the present invention to provide a water-based catalyst ink which contains no toxic and/or readily inflammable solvents and which in addition overcomes the disadvantages of the water-based ink previously described in EP 0 731 520 A1 (poor adhesion, poor electrical performance, short screen times). The use of this novel ink should guarantee high production safety in the area of occupational health and safety and protection of the environment and be particularly suitable for screen printing.

The object is achieved by an ink for producing electrodes for PEM fuel cells which contains a catalyst material, an ionomer, water and an organic solvent (co-solvent). The ink is characterised in that the organic solvent is at least one compound from the group of linear dialcohols with a flash point higher than 100°C and is present in the ink in a concentration between 1 and 50 wt.%, with respect to the weight of water.

Linear dialcohols are understood to be dihydric alcohols which have two hydroxyl groups in their linear, chain-shaped, molecular structure. The hydroxyl groups must not be adjacent to each other (i.e. vicinal). The chain structure may consist of aliphatic CH₂ groups, optionally with oxygen atoms (ether bridges) in between these. Possible organic solvents for catalyst inks according to the invention are, for example:

Ethylene glycol (1,2-ethanediol)	Flash point 111°C
Diethylene glycol	Flash point 140°C
1,2-propylene glycol (1,2-propanediol)	Flash point 101°C
1,3-propylene glycol (1,3-propanediol)	Flash point 131°C
Dipropylene glycol	Flash point 118°C
1,3-butanediol	Flash point 109°C
1,4-butanediol	Flash point 130°C

and other compounds from this group. Determination of the flash point is performed in a closed crucible using the Pensky-Martens method as described in accordance with European standard EN 22719 (1994). The data are taken from the database CHEMSAFE (Dechema e.V.) and represent "recommended values".

These solvents are generally soluble in or miscible with water and are hydrologically and toxicologically largely harmless. Thus, ethylene glycol, propylene glycols and butylene glycols do not have to be labelled as hazardous. Their use in industrial drying units does not represent a problem.

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According to one embodiment, the present invention provides an ink for producing a membrane electrode unit for a PEM fuel cell, comprising an electrocatalyst material, a proton-conducting ionomer, water as the main component and a water-soluble or water-miscible organic solvent, wherein the water-soluble or water-miscible organic solvent is one or more linear dialcohols with a flash point higher than 100°C and is present in the ink in a concentration of between 5 and 25 wt.%, with respect to the weight of water.

According to another embodiment, an ink of the present invention is used in the production of a membrane coated with an electrocatalyst, a membrane electrode unit or a gas distributor substrate coated with an electrocatalyst for a PEM fuel cell.

It has been shown that an ink which contains substantially water as solvent has surprisingly good adhesion to the polymer membrane when it contains, as additional solvent, 1 to 50 wt.%, preferably 5 to 25 wt.%, (with respect to the water content of the ink) of a compound from the group of linear dialcohols with flash points higher than 100°C. In addition, these inks have a very good pot life with regard to screen printing and good electrical performance values in the PEM fuel cell. Obviously, linear dialcohols have the effect of bringing about intimate contact between the catalyst layer and the ionomer membrane and thus producing good adhesion and electrical performance.

10 Since, in the ink according to the invention, the main component is still water (proportion of solvent preferably 5 – 25 wt.% with respect to the water content) and the linear dialcohols have a flash point higher than 100 °C, the known problems of ready inflammability and low ignition points associated with inks containing traditional solvents do not occur.

15 Thus, high production safety is achieved when processing these inks. In addition, a long screen life is enabled during use in screen printing processes and this clearly exceeds that of pure water-based pastes (according to EP 0 731 520 A1).

To prepare the paste, ink or preparation according to the invention, the components

- noble metal-containing supported catalyst (e.g. 40% Pt on conductivity carbon black)
- 20 - ionomer solution in aqueous form (e.g. aqueous Nafion solution)
- fully deionised water
- additional, organic solvent (cosolvent)

are weighed into a suitable container and dispersed. Devices used as dispersing equipment are those which produce a high shear force (dissolver, roll mill, etc.).

25 The ink according to the invention is applied directly to a polymer electrolyte membrane. However, it may also be applied to the gas distributor structure (e.g. carbon paper or carbon fabric). Various coating processes such as spraying, screen printing, stencil printing or off-set printing can be used for this purpose. Suitable coating processes are described in US 5,861,222.

30 The polymer electrolyte membrane consists of a proton-conducting film. Such a material is sold as a film, for example, by E.I. DuPont under the tradename Nafion®. In addition, the ionomer is also obtainable in aqueous solution with low molecular weight

aliphatic alcohols (Fluka, Buchs; Aldrich, Steinheim). Aqueous solutions of the ionomer at higher concentrations (10 %, 20 %) can be prepared from these. In principle, however, any other, in particular fluorine-free, ionomer materials, such as sulfonated polyetherketones, arylketones or polybenzimidazoles, may also be used as a film or as a
5 solution.

Any electrocatalysts known from the field of fuel cells may be used as catalysts. In the case of supported catalysts, a finely divided, electrically conductive carbon is used as the support. Carbon black, graphite or active carbon are preferably used. The platinum group metals are used as catalytically active components, e.g. platinum, palladium,
10 ruthenium and rhodium or alloys thereof. The catalytically active metals may contain further alloying additives such as cobalt, chromium, tungsten, molybdenum, vanadium, iron, copper, nickel etc. Depending on the thickness of the electrode layer, concentrations per unit area of metal in the reaction layers between 0.01 and 5 mg noble metal/cm² are possible. To prepare reaction layers, platinum electrocatalysts on carbon
15 black (Pt/C) with 5 to 80 wt.% platinum, or else support-free catalysts such as, for example, platinum black or platinum powder with high surface areas may also be used. Suitable electrocatalysts are described in patent documents EP 0 743 092 and DE 44 43 701.

Apart from these components, the ink according to the invention may also contain
20 additives such as wetting agents, flow control agents, defoaming agents, pore-producers, stabilisers, pH modifiers and other substances.

To determine the electrical performance, the membrane electrode unit prepared using the catalyst inks is tested in a PEM full cell test. The PEM cell is operated with hydrogen and air at atmospheric pressure (about 1 bar) and the characteristics (change
25 in voltage with current density) are determined. From these characteristics, the cell voltage reached with a current density of 500 mA/cm² is determined as a measure of the electrocatalytic efficiency of the cell. For better comparability of the ink systems, the catalyst load is kept constant (total load about 0.2 to 0.6 mg Pt/cm²).

The ink according to the invention can be processed effectively in different coating
30 processes and has very good adhesion to all commonly used polymer electrolyte membranes (ionomer films such as, for example, Nafion® or Flemion®). The membrane electrode units produced therewith exhibit high electrical performance in the PEM fuel cell. The electrical performance is typically well above that of a pure water-based paste.

The following examples are intended to explain the invention in more detail. Figure 1 shows the variation in cell voltage with current density for the membrane electrode units produced in comparison example 1 and example 1 using the ink according to the invention.

5 **Comparison example 1:** (Ink according to EP 0 731 520 A1)

The following components were weighed out and homogenised in a dispersing unit:

15.0 g	Pt supported catalyst (40% Pt/C, Degussa-Hüls)
50.0 g	Nafion® solution (10 % in water)
35.0 g	water (fully deionised)
100.0 g	

10 The ratio by weight of catalyst to Nafion® in this ink was 3:1. The ink was applied in a screen printing process to the anode and cathode faces of an ionomer membrane Nafion® 112 (DuPont) in the form of a square with an edge length of 7.1 cm (active cell area 50 cm²) and then dried at 80°C. Adhesion of the catalyst layers to the ionomer membrane proved to be inadequate, in particular there was loosening of the electrode layers in some places after drying and then moistening the ionomer membrane with water.

15 After drying and moistening with water, the MEU was placed between two gas distributor substrates (TORAY carbon paper, thickness 225 µm) and measurements were made in a PEM full cell operating with hydrogen/air. With a current density of 500 mA/cm² a cell voltage of 560 mV was measured (see fig. 1, type A). The total Pt load (anode and cathode) was 0.6 mg Pt/cm².

Example 1:

20 Differently from comparison example 1, the amount of water was reduced to 27 g and replaced by 8 g of dipropylene glycol in accordance with the invention:

15.0 g	Pt supported catalyst (40% Pt/C, Degussa-Hüls)
50.0 g	Nafion® solution (10 % in water)
27.0 g	water (fully deionised)
8.0 g	dipropylene glycol
100.0 g	

The ratio by weight of catalyst to Nafion® was 3:1. The proportion of dipropylene glycol was 11 wt.% (with respect to the total water content). The ink was applied to the anode and cathode faces of the ionomer membrane Nafion® 112 as described in comparison example 1. Adhesion of the electrode layers to the membrane after drying and moistening with water was very good, no loosening of the layers was observed. The total Pt load was 0.6 mg Pt/cm². The MEU produced in this way was measured in the PEM full cell test. With a current density of 500 mA/cm² a cell voltage of 634 mV was measured. This value was about 70 mV above the cell voltage in comparison example 1 (see figure 1). Thus the ink according to the invention is clearly superior to the ink in accordance with comparison example 1.

Example 2:

The following components were weighed out and homogenised:

15.0 g	PtRu supported catalyst (40% PtRu/C: 26.4% Pt, 13.6% Ru; catalyst according to US 6,007,934)
60.0 g	Nafion® solution (10 % in water)
15.0 g	water (fully deionised)
10.0 g	ethylene glycol
100.0 g	

The ratio by weight of catalyst to Nafion® was 2.5:1. The proportion of ethylene glycol was 14.5 wt.% (with respect to the total water content). The ink was applied to the anode face of an ionomer membrane (Nafion® 112, DuPont) and then dried at 80°C. Then the ink according to the invention from example 1 was applied to the rear face of the membrane (cathode face) and again dried. After drying, the MEU was moistened with water and then placed moist between two gas distributor substrates. Adhesion of the catalyst layers to the membrane was very good. Measurements were performed in the PEM full cell operating with hydrogen/air. At 500 mA/cm² a cell voltage of 620 mV was measured. The MEU also had very good performance values when operating with reformat (gas composition 60 vol.% hydrogen, 25 vol.% carbon dioxide, 15 vol.% nitrogen, 40 ppm carbon monoxide); 600 mV at 500 mA/cm².

Example 3:

Another ink was prepared, with the following composition:

15.0 g	Pt supported catalyst (40 % Pt/C, Degussa-Hüls)
50.0 g	Nafion® solution (10 % in water)
20.0 g	water (fully deionised)
15.0 g	diethylene glycol
100.0 g	

The ratio of catalyst to Nafion® was 3:1. The proportion of diethylene glycol was 23 wt.% (with respect to total water content). The ink was applied to the front and rear faces of an ionomer membrane (thickness 30 µm). Adhesion of the catalyst layers after drying and moistening with water was very good. The performance in a PEM full cell operating with hydrogen/air was 650 mV with a current density of 500 mA/cm².

Example 4:

The ink according to example 2 was applied by screen printing to a gas distributor structure which had been provided with a carbon black levelling layer and then dried at 80°C. The load on the anode gas distributor prepared in this way was 0.3 mg Pt/cm² and 0.15 mg Ru/cm². The active cell area was 50 cm². In a second step, the ink according to example 1 was applied to a gas distributor structure, again using screen printing, and dried. The cathode gas distributor prepared in this way had a load of 0.4 mg Pt/cm². To produce a membrane electrode unit, a dry ionomer membrane (Nafion 112, DuPont) was introduced in between the anode and cathode gas distributors and compression moulded at 135°C with a pressure of 7 kN. The structure produced in this way was mounted in a PEM fuel cell and measured when operating with reformat/air (gas composition; see example 2). The cell voltage was 630 mV with a current density of 500 mA/cm².

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An ink for producing a membrane electrode unit for a PEM fuel cell, comprising an electrocatalyst material, a proton-conducting ionomer, water as the main component and a water-soluble or water-miscible organic solvent, wherein the water-soluble or water-miscible organic solvent is one or more linear dialcohols with a flash point higher than 100°C and is present in the ink in a concentration of between 5 and 25 wt.%, with respect to the weight of water.
2. An ink according to claim 1, wherein the water-soluble or water-miscible organic solvent is an ethylene glycol, a diethylene glycol, a propylene glycol, a dipropylene glycol, a butanediol or any combination thereof.
3. Use of the ink as defined in claim 1 or 2, to produce a membrane coated with an electrocatalyst for a PEM fuel cell.
4. Use of the ink as defined in claim 1 or 2, to produce a membrane electrode unit for a PEM fuel cell.
5. Use of the ink as defined in claim 1 or 2, to produce a gas distributor substrate coated with an electrocatalyst for a PEM fuel cell.
6. The ink according to claim 1 or 2, wherein said linear dialcohol is 1,2-propylene glycol or 1,3-propylene glycol.
7. The ink according to claim 1 or 2, wherein said electrocatalyst is a noble metal containing a supported catalyst.
8. The ink according to claim 1 or 2, wherein the proton-conducting ionomer is employed as an ionomer solution in an aqueous form.

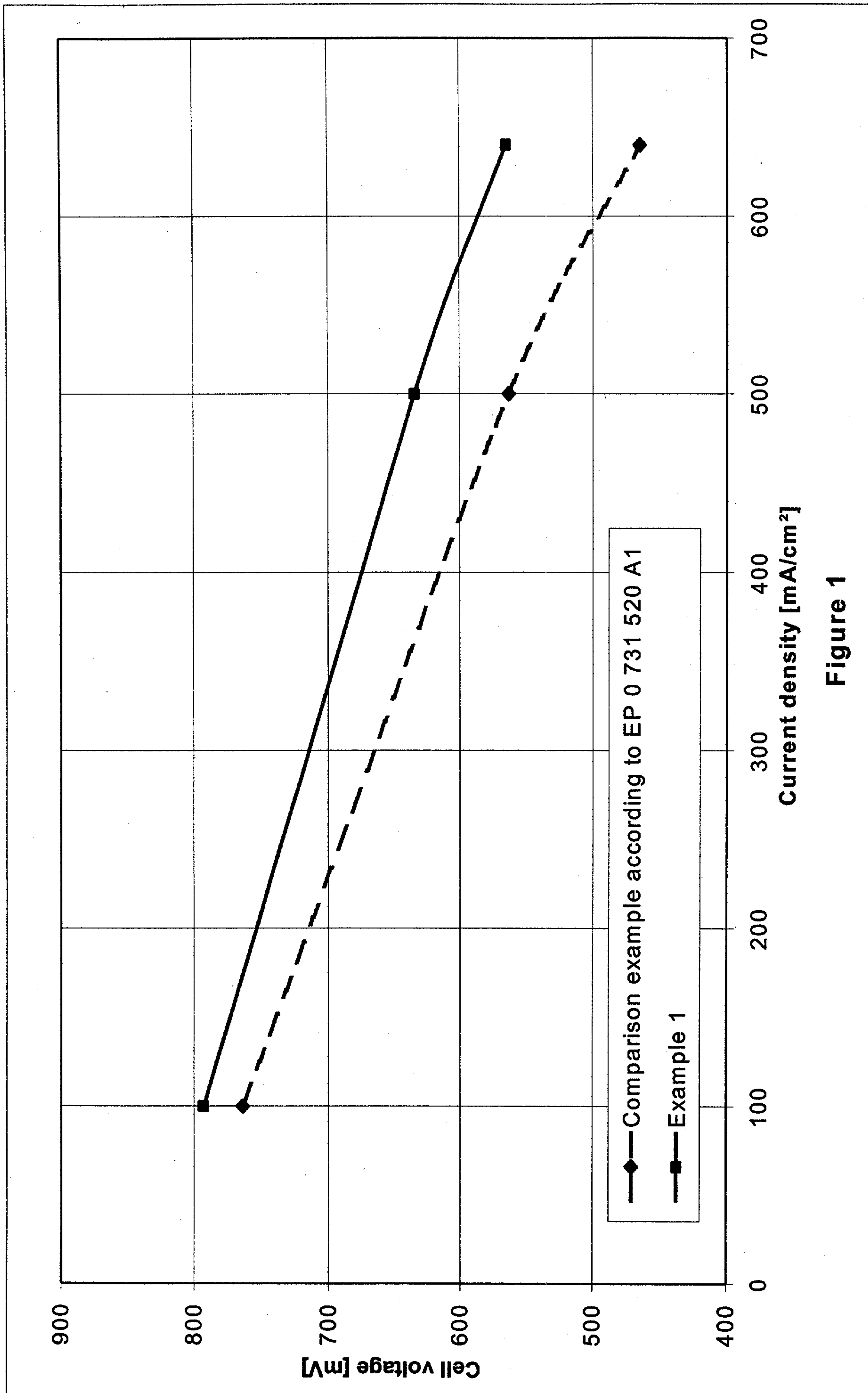


Figure 1

Marks & Clerk

