Title: PLATINUM AND PALLADIUM ALLOYS SUITABLE AS FUEL CELL ELECTRODES

Abstract: The present invention concerns electrode catalysts used in fuel cells, such as proton exchange membrane (PEM) fuel cells. The invention is related to the reduction of the noble metal content and the improvement of the catalytic efficiency by low level substitution of the noble metal to provide new and innovative catalyst compositions in fuel cell electrodes. The novel electrode catalysts of the invention comprise a noble metal selected from Pt and Pd alloyed with an alkaline earth metal.
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Platinum and palladium alloys suitable as fuel cell electrodes

Field of the invention

The present invention concerns electrode catalysts used in fuel cells (e.g., in proton exchange membrane (PEM) fuel cells - also known as polymer electrolyte membrane fuel cells). The invention is related to the reduction of the noble metal content and the improvement of the catalytic efficiency and stability of the catalyst by low level substitution of the noble metal to provide new and innovative catalyst compositions in fuel cell electrodes.

Background of the invention

Fuel cells combine hydrogen and oxygen without combustion to form water and to produce direct current electric power. The process can be described as reverse electrolysis. Fuel cells have potential for stationary and portable power applications; however, the commercial viability of fuel cells for power generation in stationary and portable applications depends upon solving a number of manufacturing, cost, and durability problems.

Electrochemical fuel cells convert fuel and an oxidant to electricity and a reaction product. A typical fuel cell consists of a membrane and two electrodes, called a cathode and an anode. The membrane is sandwiched between the cathode and anode. Fuel, such as hydrogen, is supplied to the anode, where an electrocatalyst catalyzes the following reaction: $2H_2 \rightarrow 4H^+ + 4e^-$.

At the anode, hydrogen separates into hydrogen ions (protons) and electrons. The protons migrate from the anode through the membrane to the cathode. The electrons migrate from the anode through an external circuit in the form of an electric current. An oxidant, in the form of oxygen or oxygen-containing air, is supplied to the cathode, where it reacts with the hydrogen ions that have crossed the membrane and with the electrons from the external circuit to form liquid water as the reaction product. The reaction is typically catalyzed by the platinum metal family. The reaction at the cathode occurs as follows: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$. 
The successful conversion of chemical energy into electrical energy in a primitive fuel cell was first demonstrated over 160 years ago. However, in spite of the attractive system efficiencies and environmental benefits associated with fuel-cell technology, it has proven difficult to develop the early scientific experiments into commercially viable industrial products. Problems have often been associated with lack of appropriate materials that would enable the cost and efficiency of electricity production to compete with existing power technology.

Proton exchange membrane fuel cells have improved significantly in the past few years both with respect to efficiency and with respect to practical fuel cell design. Some prototypes of fuel-cell replacements for portable batteries and for automobile batteries have been demonstrated. However, problems associated with the cost, activity, and stability of the electrocatalyst are major concerns in the development of the polymer electrolyte fuel cell. For example, platinum (Pt)-based catalysts are the most successful catalysts for fuel cell and other catalytic applications. Unfortunately, the high cost and scarcity of platinum has limited the use of this material in large-scale applications. The development of low temperature polymer electrolyte membrane fuel cells is furthermore severely hampered by the fact that the oxygen reduction reaction (ORR) is slow, resulting in low catalytic activities, even using platinum as a catalyst.

In addition, a problem with the use of platinum at the anode has been the poisoning of the catalyst surface by carbon monoxide impurities. On the cathode side, usually higher catalyst loadings have been utilised because methanol and other carbon containing fuel passing through the membrane react with oxygen at the cathode under catalytic effect of platinum, thereby decreasing the efficiency of the fuel cell.

To improve the catalytic efficiency and reduce the cost, other noble metals and non-noble metals are used to form Pt alloys as catalysts. Noble metals including Pd, Rh, Ir, Ru, Os, Au, etc. have been investigated. Non-noble metals including Sn, W, Cr, Mn, Fe, Co, Ni, Cu (U.S. Pat. No. 6,562,499) have also been tried. Different Pt-alloys were disclosed as catalysts for fuel cell applications. Binary alloys as catalysts include Pt-Cr (U.S. Pat. No. 4,316,944), Pt-V (U.S. Pat. No. 4,202,934), Pt-Ta (U.S. Pat. No. 5,183,713), Pt-Cu (U.S. Pat. No. 4,716,087), Pt-
Ru (U.S. Pat. No. 6,007,934), Pt-Ti, Pt-Cr, Pt-Mn, Pt-Fe, Pt-Co, Pt-Ni, Pt-Cu (GB 2 242 203). Ternary alloys as catalysts include Pt-Ru-Os (U.S. Pat. 5,856,036), Pt-Ni-Co, Pt-Cr-C, Pt-Cr-Ce (U.S. Pat. No. 5,079,107), Pt-Co-Cr (U.S. Pat. No. 4,711, 829), Pt-Fe-Co (U.S. Pat. No. 4,794,054), Pt-Ru-Ni (U.S. Pat.-No. 6,517,965), Pt-Ga-(Cr, Co, Ni) (U.S. Pat. No. 4,880,711), Pt-Co-Cr (U.S. Pat. No. 4,447,506). Quaternary alloys as catalysts include Pt-Ni-Co-Mn, (U.S. Pat. No. 5,225,391), Pt-Fe-Co-Cu (U.S. Pat. No. 5,024,905).

Furthermore, alloys of Pt or Pd with Sc, Y, or La suitable electrodes in a fuel cell are disclosed in WO 2011/006511. Pt₃Y, Pt₅Y, and Pt₅La are, in that order, the most active of the alloys tested therein. Pt₃Y, Pt₅Y, Pt₅La, and Pt₅La are further discussed as electrocatalysts by Greeley et al., Nature Chemistry, 2009, 1, 552; Stephens et al., ChemCatChem 2012, 4, 341; Stephens et al. Energy Environ. Sci. 2012, 5, 6744; and Yoo et al. (Energy Environ. Sci. 2012, 5, 7521).

Escudero-Escribano et al. (J Am. Chem. Soc. 2012, 134, 16476) discuss the activity and stability of Pt₅Gd as an electrocatalyst. None of these disclose or suggest, however, alloying with alkaline earth metals.

However, for the PEM fuel cell to become a viable technology, there is still a need to increase the catalytic activity, increase stability of the catalyst, and/or decrease the cost of the electrodes. Since the cost of the expensive ion conducting membrane separating the electrodes scales with the geometric area/active-site density of the electrode, the reduction of cost by using cheaper but less active electrodes with lower active-site density would be offset by the increasing cost of the membrane. Moreover, a decreased active-site density cannot be offset by utilizing an electrode with a greater thickness: this would also impede the transport of reactive gases. As an example, reference should be made to the so-called Fe/C/N electrodes as disclosed inter alia by Lefevre et al., Science, 324, 71(2009). They have turnover frequencies, i.e. the number of electrons produced per active site per second, comparable to platinum electrodes, but still have lower active-site density.

Japanese patent application JP 10 214630 A discloses the use of binary alloys containing noble metals and rare earth metals in polymer electrolyte fuel cells.
Alkaline earth metals are found in group IIA of the periodic table of the elements and are generally considered very reactive elements. Calcium, strontium and barium metal react readily with water at room temperature. Thus, the presence of these elements as a stabilizing factor in a non-ionic substance, such as a metal alloy, is counter-intuitive to the skilled person. Alkaline earth metals are very abundant in nature and come at a relatively low cost compared to other metals.

US 4,186,110 discloses a ternary Pt-Sr-Ti alloy prepared by heating Pt and SrTiCb. However, this alloy only displayed a 20% increase in activity compared to pure platinum.

It is an object of the invention to provide an electrode alloy material with an increased catalytic activity towards oxygen reduction compared to pure platinum and an increased stability under normal operating conditions. It is furthermore an object of the invention to provide an electrode alloy with a lower cost compared to pure platinum while retaining a comparable active-site density. Another object of the invention is to provide an electrode alloy material whose activity enhancement over Pt is stable over extended periods of time.

**Summary of the invention**

The inventors of the present invention have found that the above described objects may be achieved by one aspect of the invention by providing an electrode comprising an alloy containing one or more noble metals selected from Pd, Pt and mixtures thereof, and at least one alkaline earth metal, wherein said alloy is supported on a conductive support material, wherein the atomic ratio between said one or more noble metals and said at least one alkaline earth metal is in the range 1.5:1 to 10:1.

In another aspect, the invention concerns a fuel cell comprising the electrode of the present invention and an electrolyte.

In a further aspect, the invention relates to the use of an alloy according to the invention as an electrocatalyst.
In a further aspect, the invention relates to the use of an alloy according to the invention, wherein the alloy comprises a surface layer of pure noble metal - a layer described as noble metal skin (e.g. Pt skin) throughout this application.

It has been found that the electrodes of the present invention are up to four times more active than pure platinum. Furthermore, since the electrodes of the present invention are alloys with non-precious metals rather than pure platinum, the cost of the electrodes has been reduced while at the same time maintaining the active-site density.

Brief description of the drawings

Figure 1 is a schematic diagram showing a schematic of a fuel cell, in which the catalyst of the invention is used at the electrode of the fuel cell.

Figure 2 contains cyclic voltammograms for Pt, PtsCa and PtsSr.

Figure 3 shows the activity of PtsCa and PtsSr compared to that of Pt as measured by carrying out cyclic voltammograms in O2-saturated electrolyte (only the anodic sweep has been shown).

Figure 4 is a graphical representation which illustrates the specific activity as a function of the electrode potential, U, for PtsCa and PtsSr compared to that of Pt and Pt3Y, expressed as a kinetic current density, jk.

Figure 5 shows the angle-resolved XPS profile of PtsSr after the ORR, illustrating the Pt-skin formation after electrochemistry.

Figure 6 shows the specific activity of PtsCa, expressed as a kinetic current density, jk, before and after a stability test consisting of 10,000 cycles between 0.6 and 1.0 V.

Figure 7 contains X-ray diffraction traces of Pt and PtsCa.
Detailed description of the invention

Definitions and nomenclature

Alloy

An alloy is a partial or complete solid solution of one or more elements in a metallic matrix. Complete solid solution alloys give single solid phase microstructure, while partial solutions give two or more phases that may be homogeneous in distribution depending on thermal (heat treatment) history. Alloys usually have different properties from those of the component elements.

Binary alloys

In the present context, the term "binary alloy" refers to an alloy containing substantially only two metallic elements in the alloy. It is to be understood that alloys comprising said two metallic elements and impurities of other materials, such as other metals, than said two metallic elements constituting the binary alloy, wherein said impurities do not significantly alter the properties of the electrodes of the invention, e.g. the activity of the electrodes, within the normal measurement uncertainty limits applied by the skilled person, are also encompassed by the term "binary alloy". In one embodiment of the invention, the electrode comprises a binary alloy containing a noble metal selected from Pd and Pt, and an alkaline earth metal.

Intermetallic compound

In the present context, the term "intermetallic compound" refers to those alloys which exist as a single ordered phase. Alloys don't necessarily need to be ordered or a single phase.

Alkaline earth metal

In the context of the present invention, the term "alkaline earth metal" is intended to include the elements Mg, Ca, Sr, and Ba. In one embodiment, "alkaline earth metal" includes Mg, Ca, Sr, Ba, and any mixtures thereof, such as Ca, Sr, Ba, and any mixtures thereof, e.g. Ca and Sr, and any mixtures thereof, such as Ca, or such as Sr.
Electrocatalyst

In the context of the present invention, an "electrocatalyst" is a catalyst that participates in an electrochemical reaction. Catalyst materials modify and increase the rate of chemical reactions without being consumed in the process.

Electrocatalysts are a specific form of catalysts that function at electrode surfaces or may be the electrode surface itself. When an electrocatalyst functions heterogeneously, it is typically a solid, such as a planar platinum surface or platinum nanoparticles. When an electrocatalyst functions homogeneously, such as a co-ordination complex or enzyme, it will be in the liquid phase. The electrocatalysts assist in transferring electrons between the electrode and reactants and/or facilitates an intermediate chemical transformation described by overall half-reactions.

Electrochemical cell

In the context of the present invention, an "electrochemical cell" is a device used for generating an electromotive force (voltage) and current from chemical reactions, or the reverse, inducing a chemical reaction by a flow of current. The current is caused by the reactions releasing and accepting electrons at the different ends of a conductor. An "electrochemical cell" contains at least two electrodes and at least one electrolyte separating the electrodes. The electrolyte may be a liquid solution or an ion conducting membrane, which allows the passage of ions to reestablish charge neutrality over the whole cell without allowing any significant passage of electrons. Suitable electrolytes for electrochemical cells are known to the person skilled in the art. One example of a suitable electrolyte for certain types of electrochemical cells, such as a fuel cell, is Nafion®. An example of a suitable liquid electrolyte is perchloric acid.

Fuel cell

In the context of the present invention, a "fuel cell" is an electrochemical cell where the energy of a reaction between a fuel and an oxidant is converted directly into electrical energy. A typical fuel cell is illustrated in figure 1. Examples of fuels suitable for fuel cells are hydrogen gas, \( \text{H}_2 \), and methanol. A typical oxidant is oxygen gas, \( \text{O}_2 \).
Conductive support

The term "conductive support material" or "conductive support" means a solid material with a resistivity at 20 °C of at the most 700 ohm meter, preferably at the most 1 ohm meter, most preferably at the most 0.001 ohm meter. The "conductive support material" as used in the present invention is suitable for use in a fuel cell. In some of the embodiments of the invention it may be desirable that the conductive support material is permeable to gaseous molecules.

The term "conductive support material" or "conductive support" also includes non-conductive support materials with an electrode backing layer or any other means of conduction, wherein the means of conduction is attached to the non-conductive support material in a manner to bring it into contact with the electrocatalyst material to be deposited on the support material. One example of this type of "conductive support material" may be found in US 5,338,430 and US 6,040,077, both of which are incorporated herein in their entirety. US 6,040,077 discloses PEM fuel cells with Pt or Pt/Ru deposited on an organic, non-conducting support material, so-called whiskers. The whiskers are acicular nanostructures grown on a substrate. The catalyst electrodes in US 6,040,077 with the non-conductive support material are covered with ELAT™ electrode backing material for completing the electric circuit.

Anode and cathode

An electrode in an electrochemical cell, such as a fuel cell, may be referred to as either an anode or a cathode. The anode is defined as the electrode, at which electrons leave the cell and oxidation occurs, and the cathode, as the electrode at which electrons enter the cell and reduction occurs. An electrode may become either an anode or a cathode depending on the voltage applied to the cell as well as the design of the cell.

Ion conducting membrane

In order to create an electrochemical circuit in a fuel cell, the electrodes may be separated by an ion conducting membrane. The membrane separating the electrodes must allow the diffusion of ions from one electrode to the other, but must keep the fuel and oxidant gases apart. It must also prevent the flow of
electrons. Diffusion or leakage of the fuel or oxidant gases across the membrane can lead to undesirable consequences, such as short-circuiting or catalyst poisoning. If electrons can travel through the membrane, the device is fully or partially shorted out, and the useful power produced is eliminated or reduced.

Suitable ionic conducting membranes include, but are not limited to Nafion, silicon oxide Nafion composites, polyperfluorosulfonic acids, polyarylene thioether sulfones, polybenzimidazoles, alkali-metal hydrogen sulfates, polyphosphazenes, sulfonated (PPO), silicapolymer composites, organo-amino anion exchange membranes and the like.

Ion conducting membranes suitable for use in fuel cells are generally very costly and the viability of using fuel cells commercially depends, at least in part, on minimising the amount of ion conducting membranes used in the fuel cell.

Nanoparticles

In applications, such as fuel cells, the electrocatalyst of the invention may advantageously be applied in the form of nanoparticles. In general, nanoparticles have the advantage of high surface areas per weight, which make them interesting in applications where high surface areas are advantageous, such as in catalysts. In the case of very costly catalysts, said surface area to weight ratio obviously becomes even more important.

The electrocatalyst material according to the present invention may be converted into nanoparticles suitable for use in fuel cells by applying methods well known to the person skilled in the art. Examples of such methods may inter alia be found in US 5,922,487, US 6,066,410, US 7,351,444, US 2004/0115507, and US 2009/0075142.

Noble metal skin

In the context of the present invention, the term "noble metal skin" refers to the case when the alloys as used in the present invention have a relative intensity of noble metal of approximately 100% at or near the surface of the alloy, coinciding with a relative intensity of the one or more alkaline earth metals of approximately 0%, as measured by Angle Resolved X-ray Photoelectron Spectroscopy (ARXPS).
Beyond the noble metal skin, i.e. deeper into the surface of the alloy, the relative intensities of noble metal and the one or more alkaline earth metals of the alloy will approach constant values corresponding to the bulk composition of the alloy, e.g. corresponding to PtsSr.

Embodiments of the invention

The present invention concerns an electrode comprising a noble metal alloy. Noble metals are known in the art to be among the best catalysts in fuel cells. By instead using a noble metal alloy it is possible not only to decrease the cost of the electrode by substituting the very expensive noble metal with less expensive metals, but also to increase the activity of the electrode. Many efforts have been put into developing these alloys of noble metals, such as platinum and palladium, with other transition metals like Cr, Co, V, Ni. However, the operating potential at a given current density of fuel cells employing these prior art alloy catalysts decreases with time towards that of fuel cells employing pure Pt electrocatalysts. A review of some of these prior art alloy catalysts may be found in Gasteiger et al, *Appl. Catal. B-Environ* **56**, 9-35 (2005). By using the present invention, noble metal alloys comprising alkaline earth metals are surprisingly solving both problems by ensuring the stability together with an increased activity of the electrode.

It has furthermore been found that the alloys comprised in the electrodes of the invention form noble metal overlayers - so-called noble metal "skins" - at the surface of the alloy. The depth of the skin is from one to several layers of noble metal, such as 1, 2, 3, or 4 layers of noble metal, such as platinum. This is important in order to ensure stability of the electrodes under the high potentials and acidic conditions of PEM fuel cells.

The invention relates to an electrocatalyst alloy supported on a conductive support. The support serves several different purposes. First, it serves the purpose of simply supporting the catalyst material, which may be deposited on the support in a very large area in a very thin layer. This holds the advantage of minimizing the needed mass of catalyst material to cover a large surface area of
the catalyst. To optimize this effect, supports made with various surface porosities and roughness can increase the surface area of the support and hence the catalyst. Also more exotic supports, such as carbon nanotubes, have been investigated for these purposes. Furthermore, the support serves as a conducting material by providing a pathway for electronic (and in some cases ionic) conduction to and from the active sites of the catalyst. Finally, the support may also be gas permeable in order to facilitate the transport of gases to the catalyst.

In an embodiment of the invention, the noble metal used in the alloy is platinum.

Platinum has long been known to be one of the best catalysts for the cathodic reaction. One of the drawbacks is the very high cost. Several attempts to improve cost efficiency have been made, such as depositing thin layers of Pt or alloying with cheaper materials or both. By alloying according to the present invention platinum can be used in very small amounts due to the increased activity of the alloys and the cheaper costs of alkaline earth metals.

One aspect of the present invention concerns an electrode comprising an alloy containing one or more noble metals selected from Pd, Pt, and mixtures thereof, and at least one alkaline earth metal, wherein said alloy is supported on a conductive support material, and wherein the atomic ratio between said one or more noble metals and said at least one alkaline earth metal is in the range 1.5:1 to 10:1.

The noble metal of the alloy may be either platinum or palladium, as well as any mixture thereof. In one embodiment, the noble metal is substantially pure platinum. In another embodiment, the noble metal is substantially pure palladium. In the embodiment of the invention, wherein the alloy contains a mixture of platinum and palladium, the mixture may comprise platinum and palladium in any ratio, such as in the atomic ratio 1:1.

In the context of the present invention, when referring to substantially pure metals or alloys, such as "substantially pure platinum", it is meant to encompass pure metals or alloys with a degree of impurities, which do not significantly alter the properties of the electrodes of the invention, e.g. the activity of the
electrodes, within the normal measurement uncertainty limits applied by the skilled person.

The alloy of the electrode according to the present invention comprises one or more further elements, one or more alkaline earth metals, which are the elements Mg, Ca, Sr, Ba, as well as any mixtures thereof. In one embodiment, said one or more alkaline earth metals are selected from the group consisting of magnesium, calcium, strontium, barium, and mixtures thereof. In another embodiment, said one or more alkaline earth metals are selected from the group consisting of calcium, strontium, barium, and mixtures thereof. In yet another embodiment, said one or more alkaline earth metals are selected from the group consisting of calcium, strontium, and mixtures thereof. In a further embodiment, said alkaline earth metal is substantially pure calcium. In another embodiment, said alkaline earth metal is substantially pure strontium.

In one embodiment of the invention, the alloy of the electrode consists of a substantially pure mixture of platinum and calcium. In another embodiment of the invention, the alloy of the electrode consists of a substantially pure mixture of platinum and strontium. In yet another embodiment, the alloy of the electrode consists of a substantially pure mixture of platinum and barium.

As mentioned above, the invention also concerns electrodes comprising alloys of mixtures of noble metals and/or further alkaline earth metals. Said alloys may therefore also be ternary alloys or quaternary alloys. Mixtures of five or more metals are also contemplated as being encompassed by the present invention. However, in a presently preferred embodiment, said alloys are binary alloys.

In the electrode of the invention, the ratio between the one or more noble metals and the one or more further elements, the one or more non-noble metals, may vary. In a further embodiment, the present invention relates to an electrode, wherein the atomic ratio between the one or more noble metals and the one or more alkaline earth metals is in the range 8:1 to 2.5:1, e.g. in the range 6:1 to 2.8:1, such as in the range 5:1 to 3:1. In yet a further embodiment, the atomic ratio between the one or more noble metals and the one or more alkaline earth metals is in the range 3.5:1 to 2.5 to 1 or in the range 5.5:1 to 4.5:1.
Hence, the present invention encompasses an electrode comprising an alloy containing platinum and calcium with an atomic ratio in the range 10:1 to 1.5:1, such as in the range 8:1 to 2.5:1, e.g. in the range 6:1 to 2.8:1, such as in the range 5:1 to 3:1. In another embodiment, the present invention encompasses an electrode comprising an alloy containing platinum and calcium with an atomic ratio in the range 3.5:1 to 2.5:1 or in the range 5.5:1 to 4.5:1. Furthermore, the present invention encompasses an electrode comprising an alloy containing platinum and strontium with an atomic ratio in the range 10:1 to 1.5:1, such as in the range 8:1 to 2.5:1, e.g. in the range 6:1 to 2.8:1, such as in the range 5:1 to 3:1. In another embodiment, the present invention encompasses an electrode comprising an alloy containing platinum and strontium with an atomic ratio in the range 3.5:1 to 2.5:1 or in the range 5.5:1 to 4.5:1. In addition, the present invention encompasses an electrode comprising an alloy containing platinum and barium with an atomic ratio in the range 10:1 to 1.5:1, such as in the range 8:1 to 2.5:1, e.g. in the range 6:1 to 2.8:1, such as in the range 5:1 to 3:1. In another embodiment, the present invention encompasses an electrode comprising an alloy containing platinum and barium with an atomic ratio in the range 3.5:1 to 2.5:1 or in the range 5.5:1 to 4.5:1.

In yet a further embodiment, the present invention relates to an electrode, wherein the alloy is Pt5Sr. In the context of the present invention, the term "Pt5Sr" is a mixture of Pt and Sr with the atomic ratio 5:1. The skilled person may, while measuring the composition of an electrode according to this embodiment of the invention, arrive at a measured ratio deviating slightly from the exact ratio 5:1. It is however envisioned that electrodes having a measured composition substantially equal to 5:1 are also encompassed by the scope of this embodiment, as long as said deviation is within the normal uncertainty limits accepted by the person skilled in the art.

In yet a further embodiment, the present invention relates to an electrode, wherein the alloy is Pt5Ca. In the context of the present invention, the term "Pt5Ca" is a mixture of Pt and Ca with the atomic ratio 5:1. The skilled person may, while measuring the composition of an electrode according to this embodiment of the invention, arrive at a measured ratio deviating slightly from the exact ratio 5:1. It is however envisioned that electrodes having a measured
composition substantially equal to 5:1 are also encompassed by the scope of this embodiment, as long as said deviation is within the normal uncertainty limits accepted by the person skilled in the art.

In yet a further embodiment, the present invention relates to an electrode, wherein the alloy is Pt5Ba. In the context of the present invention, the term "Pt5Ba" is a mixture of Pt and Ba with the atomic ratio 5:1. The skilled person may, while measuring the composition of an electrode according to this embodiment of the invention, arrive at a measured ratio deviating slightly from the exact ratio 5:1. It is however envisioned that electrodes having a measured composition substantially equal to 5:1 are also encompassed by the scope of this embodiment, as long as said deviation is within the normal uncertainty limits accepted by the person skilled in the art.

In yet a further embodiment, the present invention relates to an electrode, wherein the alloy is Pt3Mg. In the context of the present invention, the term "Pt3Mg" is a mixture of Pt and Mg with the atomic ratio 3:1. The skilled person may, while measuring the composition of an electrode according to this embodiment of the invention, arrive at a measured ratio deviating slightly from the exact ratio 3:1. It is however envisioned that electrodes having a measured composition substantially equal to 3:1 are also encompassed by the scope of this embodiment, as long as said deviation is within the normal uncertainty limits accepted by the person skilled in the art.

In yet a further embodiment, the present invention relates to an electrode, wherein the alloy is Pt3Sr. In the context of the present invention, the term "Pt3Sr" is a mixture of Pt and Sr with the atomic ratio 3:1. The skilled person may, while measuring the composition of an electrode according to this embodiment of the invention, arrive at a measured ratio deviating slightly from the exact ratio 3:1. It is however envisioned that electrodes having a measured composition substantially equal to 3:1 are also encompassed by the scope of this embodiment, as long as said deviation is within the normal uncertainty limits accepted by the person skilled in the art.
In yet a further embodiment, the present invention relates to an electrode, wherein the alloy is Pt\textsubscript{2}Ca. In the context of the present invention, the term "Pt\textsubscript{2}Ca" is a mixture of Pt and Ca with the atomic ratio 2:1. The skilled person may, while measuring the composition of an electrode according to this embodiment of the invention, arrive at a measured ratio deviating slightly from the exact ratio 2:1. It is however envisioned that electrodes having a measured composition substantially equal to 2:1 are also encompassed by the scope of this embodiment, as long as said deviation is within the normal uncertainty limits accepted by the person skilled in the art.

In yet a further embodiment, the present invention relates to an electrode, wherein the alloy is Pt\textsubscript{2}Sr. In the context of the present invention, the term "Pt\textsubscript{2}Sr" is a mixture of Pt and Sr with the atomic ratio 2:1. The skilled person may, while measuring the composition of an electrode according to this embodiment of the invention, arrive at a measured ratio deviating slightly from the exact ratio 2:1. It is however envisioned that electrodes having a measured composition substantially equal to 2:1 are also encompassed by the scope of this embodiment, as long as said deviation is within the normal uncertainty limits accepted by the person skilled in the art.

In yet a further embodiment, the present invention relates to an electrode, wherein the alloy is Pt\textsubscript{2}Ba. In the context of the present invention, the term "Pt\textsubscript{2}Ba" is a mixture of Pt and Ba with the atomic ratio 2:1. The skilled person may, while measuring the composition of an electrode according to this embodiment of the invention, arrive at a measured ratio deviating slightly from the exact ratio 2:1. It is however envisioned that electrodes having a measured composition substantially equal to 2:1 are also encompassed by the scope of this embodiment, as long as said deviation is within the normal uncertainty limits accepted by the person skilled in the art.

As mentioned above, alloys may exist in a single ordered phase, which is referred to as an "intermetallic compound" in the present context. In a presently preferred embodiment, the alloys of the electrodes according to the invention contain at least 70% by weight intermetallic compound, such as at least 75% by weight,
80% by weight, 85% by weight, 90% by weight, or 95% by weight. In another embodiment, the alloy contains substantially only intermetallic compound.

As an example, the embodiment wherein the alloy is PtsCa may contain at least 70% intermetallic compound, i.e. at least 70% of the PtsCa is in a single ordered phase.

In a further aspect, the present invention relates to a fuel cell comprising the electrode according to the invention.

While the electrode of the invention is envisioned for use in any type of electrochemical cell, the inventors of the present invention have found that it is particularly useful in fuel cells in the conversion of chemical energy into electric energy. It has further been found that the electrodes of the present invention are especially useful in low-temperature fuel cells, i.e. fuel cells operating below 300 °C, such as in the range 0 °C to 300 °C.

The electrodes of the present invention may function either as the anode or the cathode of a fuel cell, depending on the voltage and design of the fuel cell. The electrodes of the invention are however preferably used as cathodes.

In yet a further aspect, the present invention relates to the use of the alloy as defined herein as an electrocatalyst.

In still a further aspect, the present invention relates to a method for the production of electrical energy comprising the step of supplying an oxidizable fuel, such as H2 or methanol, and an oxidant, such as O2, to a fuel cell, such as a low-temperature fuel cell, as defined herein.

The different embodiments of the present invention may be combined with any of the other embodiments.

Throughout this document the terms "comprising" or "comprises" do not exclude other possible elements or steps. Also, the mentioning of references such as "a" or "an" etc. should not be construed as excluding a plurality.
Examples

Electrodes

Each electrode was 5 mm in diameter (0.196 cm² geometric surface area). The alloys were produced as standard alloys according to techniques well known in the art of alloy production. Upon specification, several providers around the world will produce the alloys according to standard practice. One such provider is Mateck GmbH in Germany. The specification for the Pt₁Ca and PtₛSr electrodes used in these examples was: purity 99.95%, dia. 5 +/- 0.05 mm x thickness 3 +/- 0.5 mm, one side polished.

Electrochemical measurements

Within a few seconds of removing the electrode from the UHV chamber, the clean electrode was protected using a droplet of ultrapure water (Millipore Milli-Q water, 18 MΩ cm⁻¹), saturated with H₂. It was then placed face down onto a wet polypropylene film, and pressed into the arbor of a rotating disc electrode (RDE).

The electrochemical experiments were performed with Bio-Logic Instruments’ VMP2 potentiostat, controlled by a computer. The RDE assemblies were provided by Pine Instruments Corporation. A standard three-compartment glass cell was used. The cell was cleaned in a "piranha" solution consisting of a 3:1 mixture of 96% H₂SO₄ and 30% H₂O₂, followed by multiple runs of heating and rinsing with ultrapure water (Millipore Milli-Q, 18.2 MΩ cm) to remove sulphates. The electrolyte, 0.1 M HCl/NaOH (Merck Suprapur) was prepared from ultrapure water. The counter electrode was a Pt wire and the reference was a Hg/Hg₂SO₄ electrode; both were separated from the working electrode compartment using ceramic frits. Following each measurement, the potential of the reference electrode was checked against a reversible hydrogen electrode (RHE) in the same electrolyte. All potentials are quoted with respect to the RHE, and are corrected for Ohmic losses. The measurements were conducted at 23 °C. Following each measurement, 0 V vs. RHE was established by carrying out the hydrogen oxidation and hydrogen evolution reactions on Pt in the same electrolyte. The ohmic drop was measured by carrying out an impedance spectrum with a peak-to-peak amplitude of 10 mV, typically from 500 kHz down to 100 Hz. The target resistance was evaluated from the high-frequency intercept on the horizontal
(real) axis of the Nyquist plot and further checked by fitting the impedance spectra by using EIS Spectrum Analyser software. The uncompensated resistance came typically to approximately 25-30 Ω, and was independent of the potential, rotation speed and the presence of O₂.

The RDE was immersed into the cell under potential control at 0.05 V into a N₂ (N5, Air Products) saturated electrolyte. The oxygen reduction reaction (ORR) activity measurements were conducted in an electrolyte saturated with O₂ (N55, Air Products). The PtsCa and PtsSr electrodes were cycled in nitrogen-saturated electrolytes until stable cyclic voltammograms (CVs) were obtained (100-200 cycles). A typical stable CVs on sputtered-cleaned PtsCa and PtsSr are shown in Figure 2, and compared to the base CV on polycrystalline Pt. The ORR activity measurements were conducted in an electrolyte saturated with O₂ (N55, Air Products).

Angle Resolved X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface analysis technique, usually implemented ex-situ under ultra high vacuum conditions (Chorkendorff and Niemantsverdriet, Concepts of Modern Catalysis and Kinetics, 2003). When an incident X-ray beam hits the surface, photoelectrons are emitted. The binding energy of these photoelectrons is characteristic of the elemental composition and chemical state of the atoms in the surface and near surface region. Varying the angle of the photoelectron analyser with respect to the normal to the sample allows different depth scales to be probed. Thus, angle resolved XPS allows a non-destructive depth profile to be obtained.

Example 1 - Activities of the electrodes

The activity of the catalysts for the ORR was measured by carrying out cyclic voltammograms in O₂ saturated solution, shown in Fig 3. The onset for each electrode starts at ~1 V, and there is an initial exponential increase in the current, characteristic of kinetic control (i.e. where the current is not limited by diffusion). At lower potentials (~0.7 V < U < ~0.95 V), the current approaches the mixed regime, where mass transport (diffusion) plays an increasingly important role. This potential range is the most interesting for fuel cell applications, the operating
potential of fuel cells is typically in this range. At still lower potentials, the current reaches its diffusion limited value, \( \sim 5.8 \: \text{mA cm}^{-2} \). In the mixed regime, the ORR activity of different catalysts can be compared by evaluating the half wave potential, \( U_{1/2} \) (i.e. the potential at which the current reaches half its diffusion limited value). PtsSr shows a positive shift in \( U_{1/2} \) of \( \sim 40 \: \text{mV} \) and PtsCa shows a positive shift in \( U_{1/2} \) of \( \sim 50 \: \text{mV} \). These data show that it exhibits significant activity improvements over Pt. The positive shift in half wave potential means that the diffusion limited value is reached at a higher potential, i.e. that the kinetics are faster than for pure platinum.

Modern PEM fuel cells have been designed for efficient delivery of reactive gases, thus mass transport effects are only of secondary importance; electrochemical kinetics are the primary cause of inefficiency (Gasteiger et al., Appl. Catal. B-Environ., 56, 9 (2005)). In Fig. 4, the measured current density is corrected for mass transport to obtain the true kinetic current density, \( j_k \) of the catalyst, as a function of potential, \( U \).

The kinetic current density for oxygen reduction, \( j_k \), was calculated using the following equation:

\[
1/j_k = 1/j_{\text{meas}} - 1/j_d
\]

where \( j_{\text{meas}} \) is the measured current density, and \( j_d \) is the diffusion limited current density.

By extrapolation, the increase in activity is even higher at 0.7 V, the potential at which fuel cells are most commonly operated. Such a high increase in current at the same operating potential results in the increase of the output power with the same factor. This is significant in the objective of achieving commercially viable fuel cells.

Example 2 - ARXPS of PtsSr

Evidence for a noble metal skin of the alloys as employed in the present invention is provided in Fig. 5, which contains a depth profile of a PtsSr sample, constructed
from Angle Resolved X-ray Photoelectron Spectroscopy data. Figure 5 shows the depth profile after being subjected to the ORR in an electrochemical cell. Evidently, a skin was formed by exposing the catalyst surface to acidic electrolyte, where the alkaline earth metal, Sr, would dissolve spontaneously from the surface layer.

In-depth surface composition information of PtSr was extracted from AR-XPS spectra recorded using a Theta Probe instrument (Thermo Scientific). The chamber has a base pressure of $5 \times 10^{-10}$ mbar. The instrument uses monochromatised AlKα (1486.7 eV) X-rays, and the electron energy analyzer has an acceptance angle of 60°. It facilitates XPS spectra recorded from within a diameter of 15 $\mu$m with a resolution corresponding to a Ag 3ds/2 full width half maximum (FWHM) smaller than 0.5 eV. The AR-XPS spectra were obtained in parallel, without tilting the sample. In consideration of the count statistics at the grazing angles, an X-ray beam size of 400 $\mu$m and an energy resolution corresponding to approximately 1 eV Ag 3ds/2 FWHM was used.

The surface was sputter cleaned with a 0.5 keV beam of Ar$^+$ ions, with a current of 1 $\mu$A, over a 6 x 6 mm$^2$ area. This was typically continued for around 20 minutes, until the XPS measurement indicated that impurities were negligible. The XPS spectra were taken at several different locations over the metal surfaces. For the depth profiles, the electrons emitted at angles between 20° and 80° to the surface normal were analysed in parallel and detected in 16 channels corresponding to 3.75° wide-angle intervals. After XPS identification of the elements present at the surface, their main features were measured in detail with AR-XPS. The depth concentration profiles were obtained using the simulation tool, ARProcess (Thermo Avantage software), which uses a maximum entropy method combined with a genetic algorithm. In all cases, the simulations were based on the relative intensities between Pt 4f, O 1s and C 1s, and Sr 3d at each angle, up to 70.6°. The most grazing angles were omitted from the analysis to reduce the influence of diffraction effects and elastic scattering.
Example 3 - Stability of PtsCa

In order to study the stability of polycrystalline PtsCa electrodes in acidic solutions, an accelerated stability test consisting of continuous cycles from 0.6 V to 1.0 V vs. RHE in an oxygen-saturated 0.1 M HClO$_4$ electrolyte at 100 mV s$^{-1}$ and 23 °C was performed. Figure 6 shows the Tafel plots for the ORR on PtsCa before (full curve) and after (dashed curve) 10,000 cycles in the conditions described above. Interestingly, these results show that the percentage of activity loss after 10,000 cycles is approximately 23%, most of this loss occurring in the first 2000 cycles.

Example 4 - X-ray diffraction

The bulk composition of PtsCa and PtsSr was verified using X-ray diffraction (XRD), using a PANalytical X’Pert PRO instrument. The result for PtsCa is shown in Figure 7. The patterns for Pt and PtsCa corresponded to the respective reference traces for these compounds, from the powder diffraction file database.

Although the present invention has been described in connection with the specified embodiments, it should not be construed as being in any way limited to the presented examples. The scope of the present invention is set out by the accompanying claim set.
Claims

1. An electrode comprising a binary alloy containing a noble metal selected from Pd and Pt, and an alkaline earth metal, wherein said alloy is supported on a conductive support material, wherein the atomic ratio between said noble metal and said alkaline earth metal is in the range 1.5:1 to 10:1.

2. The electrode according to claim 1, wherein the noble metal is platinum.

3. The electrode according to any one of claims 1 or 2, wherein said alkaline earth metal is Ca, Sr, or Ba.

4. The electrode according to any one of the preceding claims, wherein said alkaline earth metal is Ca or Sr.

5. The electrode according to any one of the preceding claims, wherein said alkaline earth metal is Ca.

6. The electrode according to any one of claims 1 to 4, wherein said alkaline earth metal is Sr.

7. The electrode according to any one of the preceding claims, wherein the atomic ratio between said one or more noble metals and said at least one alkaline earth metal is in the range 2.5:1 to 8:1.

8. The electrode according to any one of the preceding claims, wherein the atomic ratio between said one or more noble metals and said at least one alkaline earth metal is in the range 2.8:1 to 6:1.

9. The electrode according to any one of the preceding claims, wherein the atomic ratio between said one or more noble metals and said at least one alkaline earth metal is between 3:1 and 5:1.

10. The electrode according to any one of the preceding claims, wherein said alloy is PtsSr.
11. The electrode according to any one of claims 1 to 9, wherein said alloy is PtsCa.

12. A fuel cell comprising the electrode according to any one of the preceding claims and an electrolyte.

13. The fuel cell according to claim 12, wherein the alloy of the electrode contains a noble metal skin on the surface.

14. The fuel cell according to any one of claims 12 or 13, wherein the electrolyte is an ion conducting membrane.

15. Use of the alloy according to any one of claims 1 to 11 as an electrocatalyst.
**FIG. 1**

A Fuel Cell

- **Anode Side**
  - Fuel e.g. H₂, CH₃OH
  - Porous electron conductor + Catalyst for the anodic reaction
  - Ion-conducting membrane (no electron conductivity)

- **Cathode Side**
  - Oxidizing agent e.g. O₂
  - Porous electron conductor + Catalyst for the cathodic reaction
  - Loading

**FIG. 2**

Graph showing current density (J) vs. voltage (U/V) for different catalysts.

- Pt₅Ca
- Pt₅Sr
- Pt
FIG. 3
**INTERNATIONAL SEARCH REPORT**

**PCT/DK2013/050396**

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. H01M4/38 H01M4/46 H01M4/92 H01M8/10

**ADD.**

According to International Patent Classification (IPC), as to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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Further documents are listed in the continuation of Box C. 

See patent family annex.

**Date of the actual completion of the international search**

18 February 2014

**Date of mailing of the international search report**

17/03/2014

Name and mailing address of the ISA/
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Authorized officer

Martins Lopes, Luis
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