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(54) Title: IMPROVEMENTS IN CATALYSTS

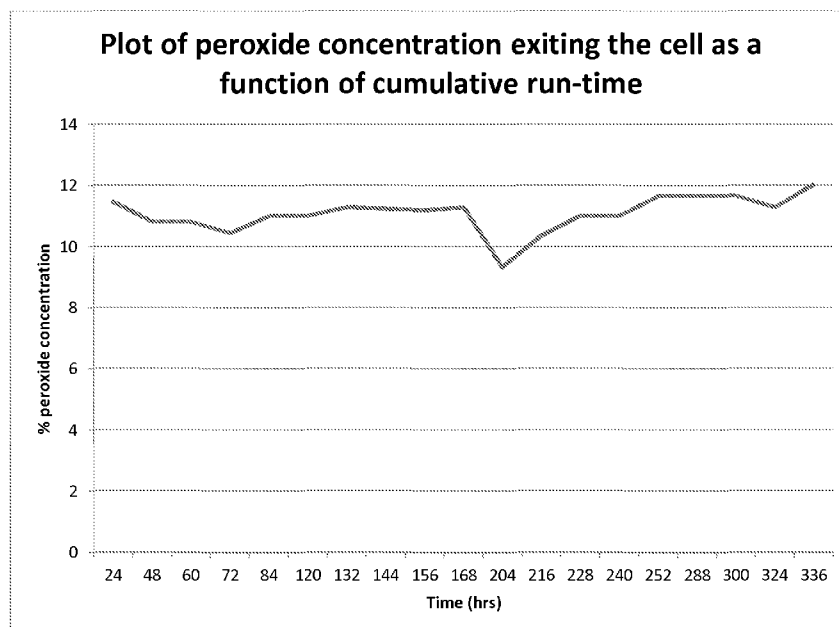


Figure 6

(57) Abstract: The invention provides an electrocatalyst suitable for use in a fuel cell for the generation of hydrogen peroxide comprising an activated transition metal-free carbon support. The invention also provides a process for the preparation of the electrocatalyst and a method for the manufacture of hydrogen peroxide.



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Improvements in Catalysts

The present invention concerns improvements in catalysts, and more especially concerns a novel metal-free electrocatalyst and its potential use in industry, particularly in the production of hydrogen peroxide.

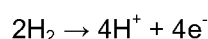
Hydrogen peroxide is used widely as an environmentally benign oxidising agent. It is used in the pulp and paper, textile and chemical industries and production is approximately 1,000,000 tonnes per annum in Europe. At present, hydrogen peroxide is manufactured mainly by a chemical route based in the reduction of an anthraquinone with hydrogen followed by its oxidation with air. The hydrogen peroxide is then extracted in an aqueous stream and must be further purified to eliminate organic contaminants. The method requires large-scale installation to be economical and the hydrogen peroxide must be transported to the point of use. The anthraquinone process carries certain environmental risks, and is energy intensive.

An electrochemical cell for hydrogen peroxide production is described in US Patents 5,565,073 and 5,647,968. Oxygen is reduced and water is oxidised in a liquid alkaline electrolyte. The process requires significant input of electrical energy, and the hydrogen peroxide is produced in an alkaline solution (generally a sodium hydroxide solution). Separation of the peroxide from the base is difficult, making the process expensive and inefficient for the production of free hydrogen peroxide. An advantage of this electrochemical process over the anthraquinone process, however, is that it does offer an opportunity to build small point-of-use hydrogen peroxide generators, if other technological problems can be overcome.

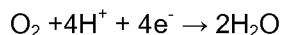
A fuel cell is fundamentally an electrochemical cell formed from two electrodes and an intervening electrolyte. In a fuel cell, the stored chemical energy of a fuel and an oxidant is converted into electrical energy. The fuel is usually hydrogen or methanol, and this is combined with oxygen to produce power. The hydrogen or methanol is oxidised at the anode and oxygen is reduced at the cathode. The electrodes are porous to gas diffusion and both are in contact with the electrolyte. The electrolyte may be a liquid or solid, acid or alkaline in nature.

There has recently been a high level of research and development in fuel cell technology. It is envisaged that fuel cells will provide power sources for a wide range of applications, particularly as a source of power for small items such as laptops or mobile phones, potentially as a replacement for internal combustion engines in vehicles, and in a combined heat and power generator for domestic or other small scale use.

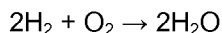
When hydrogen and oxygen are fed into a fuel cell, the reaction at the anode is the oxidation of hydrogen:



the reaction at the cathode is the four electron reduction of oxygen:

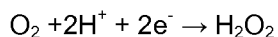


and the product of the overall reaction is water:

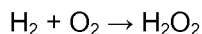


- 5 The Gibbs energy of this reaction is converted to electrical energy.

Hydrogen peroxide can be produced instead of water if the four electron reduction of oxygen is inhibited and the two electron reduction of oxygen at the cathode is promoted:



- 10 The overall cell reaction becomes:



Again, the Gibbs energy of the reaction is converted into electrical energy, so that the synthesis of hydrogen peroxide is accompanied by energy production.

- 15 Hydrogen peroxide production using fuel cell technology would provide many advantages over the current methods of manufacture of hydrogen peroxide. The process is essentially a zero-emission method and no electricity is required to power the cell; indeed energy is produced by the electrochemical cell which can be used to reduce the energy costs elsewhere, for example, in a chemical process. The generation of hydrogen peroxide can be achieved in a small modular unit that
20 can be integrated into a larger system. Accordingly, hydrogen peroxide can be generated at the point of use and there are no transportation costs or difficulties.

- Two distinct approaches have so far been adopted in the development of fuel cells for hydrogen peroxide production. One approach is similar to that adopted in the $\text{O}_2/\text{H}_2\text{O}$ electrochemical cells. A
25 wide variety of electrode surfaces such as carbon, gold and compounds of cobalt are known to promote two electron oxygen reduction in alkaline media, so a liquid alkaline electrolyte is used. An oxygen diffusion electrode is combined with a hydrogen diffusion electrode, and the hydrogen peroxide is produced in the alkaline (usually hydroxide) solution. The generation of hydrogen peroxide in an alkaline fuel cell is described in J. Electrochem. Soc., 1995, 145(10), 3444-3449.

- 30 Another approach has followed current fuel cell technology and uses a solid membrane electrolyte. In proton exchange membrane fuel cells (PEMFC), the electrolyte is a solid, proton-conducting polymer electrolyte membrane. The combined structure of a membrane and two gas diffusion electrodes is known as the membrane electrode assembly (MEA). Electrocatalysts may be incorporated on either
35 side of the membrane in the MEA to increase the rates of the desired electrode reactions. Membrane electrolytes are usually more convenient than liquid electrolytes as they are light and compact, and there are no problems with separating the product from the electrolyte. The most common membranes are based on polymeric perfluorosulfonic acid e.g. the commercially available Nafion®. EP853687B and EP758264B (both to The Dow Chemical Company) describe an electrochemical cell
40 for hydrogen peroxide synthesis containing a Nafion® based membrane. The choice of cathode

electrocatalyst is limited because most known oxygen reduction catalysts appear to promote the four electron reduction of oxygen in acidic media. Electrocatalysts based on metals such as zinc, gadolinium and lanthanum have been proposed because they appear to favour the two electron reduction. Despite careful catalyst choice, however, the selectivities of the disclosed processes are quite poor (generally below 70%) and only very weak solutions of hydrogen peroxide in water are produced (up to about 4wt%). In addition, it is likely that the integrity of catalyst materials such as zinc would be damaged by the highly acidic electrolyte environment (acid concentrations of over 3mol/l prevail in the polymer).

There remains a need for a stable electrocatalyst that will be effective for the production of hydrogen peroxide using a PEMFC structure. Additionally, it would be desirable for the electrocatalyst to be stable in the sense that after several months of stop-start operation, there would be no significant movement of catalytic material into the membrane or onto the other electrode.

Summary of the invention

In one aspect, the present invention provides an electrocatalyst suitable for use in a fuel cell for the generation of hydrogen peroxide comprising an activated transition metal-free carbon support. Preferably, the activated transition metal-free carbon support comprises a nitrogen-containing layer formed on the surface thereof.

In another aspect, the invention provides a process for the preparation of the electrocatalyst, comprising the steps of:

- (a) contacting a carbon support with a solution of an activating agent in a solvent, wherein the activating agent comprises at least one nitrogen-containing functional group;
- (b) optionally washing the product of step (a) one or more times; and
- (c) drying and heat treating the product of step (a) or step (b) under an non-oxidising atmosphere to form the electrocatalyst.

It will be understood that the electrocatalyst prepared by the above method is preferably transition metal-free. Preferably, the method does not include a step of purposefully providing (e.g. adsorbing) transition metal to the carbon support.

The nitrogen-containing functional group may be, for example, an amino group, a nitro group or an amine oxide group. Preferably, the nitrogen containing functional group is an amino group.

In yet another aspect, the present invention provides a method for the generation of hydrogen peroxide comprising the use of the electrocatalyst as defined or prepared herein in a fuel cell.

In another aspect, the present invention provide a fuel cell comprising the electrocatalyst as defined or prepared herein, as well as a sanitising device comprising said fuel cell. The present invention

further provides use of a fuel cell according to the present invention for the generation of hydrogen peroxide.

In a still further aspect, the present invention provides a method for the manufacture of an electrode for a fuel cell for the production of hydrogen peroxide, the method comprising preparing an electrocatalyst by a method comprising the steps of

- (a) contacting a carbon support with a solution of an activating agent in a solvent, wherein the activating agent comprises at least one nitrogen-containing functional group;
- (b) optionally washing the product of step (a) one or more times; and
- (c) drying and heat treating the product of step (a) or step (b) under an non-oxidising atmosphere to form the electrocatalyst,

and preparing an electrode incorporating said electrocatalyst. Preferably, the electrode is a cathode.

The present invention also provides a method for the manufacture of a fuel cell, the method comprising preparing an electrode as set out above, and incorporating the electrode into a fuel cell. Preferably, the fuel cell is a PEM-type fuel cell.

Definitions

The point of attachment of a moiety or substituent is represented by “-”. For example, -NH₂ is attached through the nitrogen atom.

A “transition metal-free electrocatalyst” refers to an electrocatalyst where a transition metal (for example, cobalt) has not been purposely adsorbed onto the carbon support. In this respect, it is irrespective whether the metal is in the form of the elemental metal, an alloy or a complex. It will be readily understood by the skilled reader that trace amounts of transition metal may inevitably be present in the electrocatalyst. Typically, the electrocatalyst includes less than 0.5 wt% transition metal, e.g. less than 0.1 wt% transition metal or less than 0.01 wt% transition metal.

“Alkyl” refers to a straight-chain, branched or cyclic saturated hydrocarbon group. In certain embodiments, the alkyl group may have from 1-20 carbon atoms, in certain embodiments from 1-15 carbon atoms, in certain embodiments, 1-8 carbon atoms. The alkyl group may be unsubstituted or substituted. Unless otherwise specified, the alkyl group may be attached at any suitable carbon atom and, if substituted, may be substituted at any suitable atom. Typical alkyl groups include but are not limited to methyl, ethyl, n-propyl, iso-propyl, cyclopropyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, cyclobutyl, n-pentyl, cyclopentyl, n-hexyl, cyclohexyl and the like.

“Aryl” refers to an aromatic carbocyclic group. The aryl group may have a single ring or multiple condensed rings. In certain embodiments, the aryl group can have from 6-20 carbon atoms, in certain embodiments from 6-15 carbon atoms, in certain embodiments, 6-12 carbon atoms. The aryl group may be unsubstituted or substituted. Unless otherwise specified, the aryl group may be attached at

any suitable carbon atom and, if substituted, may be substituted at any suitable atom. Examples of aryl groups include, but are not limited to, phenyl, naphthyl, anthracenyl and the like.

“Arylalkyl” refers to an optionally substituted group of the formula aryl-alkyl-, where aryl and alkyl are as defined above.

“Halo” refers to -F, -Cl, -Br and -I. In certain embodiments, halo is preferably -F.

“Heteroaryl” refers to an aromatic carbocyclic group wherein one or more carbon atoms are independently replaced with one or more heteroatoms (e.g. nitrogen, oxygen, phosphorus and/or sulfur atoms). Unless otherwise specified, the heteroaryl group may be attached at any suitable atom and, if substituted, may be substituted at any suitable atom. Examples of heteroaryl groups include but are not limited to furanyl, indolyl, oxazolyl, pyridinyl, pyrimidinyl, thiazolyl, thiphenyl and the like.

“Substituted” refers to a group in which one or more (e.g. 1, 2, 3, 4 or 5) hydrogen atoms are each independently replaced with substituents which may be the same or different. Examples of substituents include but are not limited to -halo, -C(halo)₃, -R^a, -NR^aR^b, -CN; wherein R^a and R^b are independently selected from the groups consisting of alkyl, aryl, arylalkyl, and wherein R^a and R^b may be unsubstituted or further substituted as defined herein.

Detailed description

The present inventors have discovered an electrocatalyst which overcomes the problems identified in the prior art. In one aspect therefore the present invention provides an electrocatalyst suitable for use in a fuel cell for the generation of hydrogen peroxide comprising an activated transition metal-free carbon support.

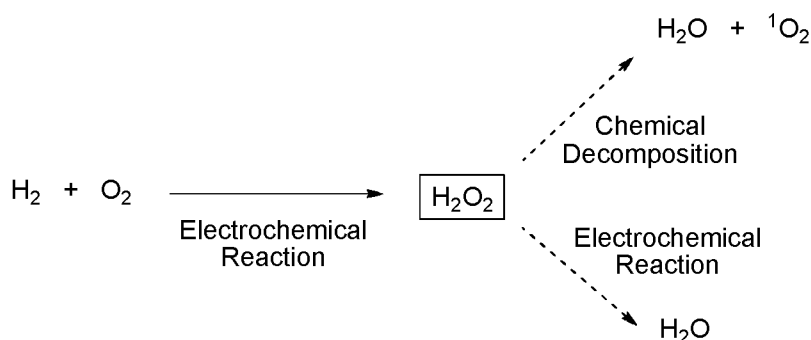
The present electrocatalyst exhibits a number of advantages over the prior art electrocatalysts. Firstly, the electrocatalyst of the invention is a transition-metal free electrocatalyst. This is beneficial as, during use in a fuel cell, there is no metal present which may leach from the electrocatalyst into the proton exchange membrane (if present), the other electrode or the outside environment if the hydrogen peroxide is being generated at the point of use.

Secondly, the present electrocatalyst may be used in acidic electrolytic environments, which is advantageous as the electrocatalyst permits peroxide generation in low pH environments. In one embodiment, the electrocatalyst may be used in an electrolytic environment of from about pH 0 to about pH 7.0. In one embodiment, the pH is ≤ about 7.0. In another embodiment, the pH is ≤ about 6.5. In yet another embodiment, the pH is ≤ about 6.0. In another embodiment, the pH is ≤ about 5.5. In yet another embodiment, the pH is ≤ about 5.0. In another embodiment, the pH is ≤ about 4.5. In yet another embodiment, the pH is ≤ about 4.0. In another embodiment, the pH is ≤ about 3.5. In yet another embodiment, the pH is ≤ about 3.0. In another embodiment, the pH is ≤ about 2.5. In yet

another embodiment, the pH is $\leq$ about 2.0. In another embodiment, the pH is $\leq$ about 1.5. In yet another embodiment, the pH is $\leq$ about 1.0. In another embodiment, the pH is $\leq$ about 0.5.

Thirdly and without wishing to be bound by theory, the present electrocatalyst appears to be selective for the 2-electron mechanism i.e. the electrocatalyst appears to be selective for the preparation of hydrogen peroxide and not water. This is advantageous as some prior art catalysts flip-flop between the 2-electron and 4-electron mechanisms depending on the temperatures at which they are heat treated.

Fourthly and without wishing to be bound by theory, the present inventors believe that the electrocatalysts of the invention exhibit preferential electrochemical activity and reduced chemical decomposition activity in situ during use in a fuel cell. This is in contrast to some prior art electrocatalysts where there appears to be a relationship between the ability of the catalysts to chemically decompose hydrogen peroxide and their ability to generate the hydrogen peroxide electrochemically in the first place.



In respect of metal-containing electrocatalysts, in particular, the metal species present in the catalysts may chemically decompose hydrogen peroxide whether the species are bound to the solid support or have been released from the solid support due to e.g. leaching. The free metal species in the latter case have been found to be active agents in their own right and can present a significant problem to be overcome.

The electrocatalyst of the present invention may be prepared according to the process comprising the steps of:

- (a) contacting a carbon support with a solution of an activating agent in a solvent, preferably a protic solvent, wherein the activating agent comprises at least one nitrogen-containing functional group;
- (b) optionally washing the product of step (a) one or more times; and
- (c) drying and heat treating the product of step (a) or step (b) under an non-oxidising atmosphere to form the electrocatalyst.

Without wishing to be bound by theory, the above process appears to activate the carbon support such that it becomes effective as an electrocatalyst in a fuel cell for the production of hydrogen peroxide.

5 In one embodiment, the carbon support is a high surface area carbon. In one embodiment, the carbon support has a surface area from about 10 m²/g to 2000 m²/g. In one embodiment, the surface area of the carbon support is $\geq$ about 25 m²/g. In another embodiment, the surface area of the carbon support is $\geq$ about 50 m²/g. In yet another embodiment, the surface area of the carbon support is $\geq$ about 75 m²/g. In yet another embodiment, the surface area of the carbon support is $\geq$ about 100 m²/g. In yet another embodiment, the surface area of the carbon support is $\geq$ about 125 m²/g. In yet another embodiment, the surface area of the carbon support is $\geq$ about 150 m²/g. In one embodiment, the surface area of the carbon support is $\leq$ about 1900 m²/g. In another embodiment, the surface area of the carbon support is $\leq$ about 1800 m²/g. In yet another embodiment, the surface area of the carbon support is $\leq$ about 1700 m²/g. In yet another embodiment, the surface area of the carbon support is $\leq$ about 1600 m²/g. In yet another embodiment, the surface area of the carbon support is $\leq$ about 1500 m²/g. . Suitable carbon supports include but are not limited to the group consisting of BP2000 (which has a surface area of about 1487 m²/g), ECJ300 (which has a surface area of about 800 m²/g), ECJ300 graphitised at 2500°C (which has a surface area of about 300 m²/g) and Vulcan XC-72R (which has a surface area of about 184 m²/g). If appropriate, the carbon support may be used alone or in combination with other carbon supports.

The activating agent preferably comprises at least one (e.g. 1, 2, 3, 4 or 5) amino groups. In one embodiment, the activating agent is selected from the group consisting of an arylamine, alkylamine and a heteroarylamine, wherein the arylamine, alkylamine and heteroarylamine independently have one or more (e.g. 1, 2, 3, 4 or 5) amino groups, and wherein the arylamine, alkylamine and heteroarylamine are independently substituted or unsubstituted. Suitable arylamines include but are not limited to aniline and phenylene diamine (o-, m- or p-). Phenylene diamine, especially o-phenylene diamine, is preferred. Suitable alkylamines include but are not limited to triethylenetetramine (TETA) and diaminooctane. Suitable heteroarylamines include but are not limited to aminopyridine (2, 3, or 4-).

The activating agent may comprise at least one (e.g. 1, 2, 3, 4 or 5) nitro groups. In one embodiment, the activating agent is selected from the group consisting of nitroaryls, nitroalkyls and nitroheteroaryls, wherein the nitroaryl, nitroalkyl and nitroheteroaryl independently have one or more (e.g. 1, 2, 3, 4 or 5) nitro groups, and wherein the nitroaryl, nitroalkyl and nitroheteroaryl are independently substituted or unsubstituted.

The activating agent may comprise at least one (e.g. 1, 2, 3, 4 or 5) amino oxide groups. In one embodiment, the activating agent is selected from the group consisting of aryl amino oxide, alkyl amino oxide and heteroaryl amino oxide, wherein the aryl amino oxide, alkyl amino oxide and

heteroaryl amino oxide independently have one or more (e.g. 1, 2, 3, 4 or 5) amino oxide groups, and wherein the aryl amino oxide, alkyl amino oxide and heteroaryl amino oxide are independently substituted or unsubstituted.

5 Aromatic (aryl or heteroaryl) activating agents may be particularly suitable. Without wishing to be bound by theory, the present inventors consider that π bonding of the nitrogen functional group-containing species may assist in forming the activated carbon support. It also may be particularly preferable that activating agent comprises two nitrogen-containing functional groups (e.g. two amino groups) which are arranged ortho to each other.

10 Any suitable quantity of activating agent may be used. Without wishing to be bound by theory, it is believed that the activating agent adsorbs onto the carbon support such that monolayer coverage of the carbon support is eventually obtained. As such, it may be generally convenient to use an activating agent in quantities in excess of that required for monolayer coverage. Accordingly, it will be
15 understood that the activated carbon support preferably has a nitrogen-containing layer formed on a surface thereof.

The activating agent is dissolved in a solvent to produce a solution. If necessary, the mixture of the activating agent and solvent may be heated in order to promote dissolution of the activating agent. In
20 one embodiment, the solvent is preferably a protic solvent. In another embodiment, the protic solvent comprises at least one of water and alcohols. Suitable alcohols include but are not limited to methanol, ethanol, propanol (n- or i-), butanol (n-, i- or t-), pentanols, hexanols and heptanols. In one embodiment, the protic solvent is preferably water.

25 Step (b) is optional and relates to washing the product of step (a) one or more (e.g. 1, 2, 3, 4 or 5) times so that excess solution of the activating agent may be removed from the surface of the carbon support. In one embodiment, the washing is carried out with a solvent, preferably a protic solvent, as described above. In this regard, if a protic solvent is used in step (b), it may be the same or different to that of step (a). In one embodiment, the product of step (a) is optionally washed one or more times
30 with water.

The product of step (a) or step (b) is then dried and is heat treated under a non-oxidising atmosphere to form the electrocatalyst. In one embodiment, the drying may be carried out at a temperature between about 15°C and about 100°C, such as about 80°C for a suitable period of time e.g. from
35 about 5 minutes to several hours, for example about 1 hour.

The heat treatment is suitably carried out at temperatures between about 200°C and about 1000°C. While the heat treatment may be carried out at temperatures above about 1000°C, this has generally found to be unfavourable as an electrocatalyst may be formed which favours the four-electron reduction
40 of oxygen (thus preferentially forming water) rather than the two-electron reduction mechanism (to

preferentially produce hydrogen peroxide). In one embodiment, the heat treatment is carried out at temperatures $\geq$ about 250°C, for example $\geq$ about 300°C. In another embodiment, the heat treatment is carried out at temperatures $\leq$ about 900°C, such as $\leq$ about 800°C, for example $\leq$ about 700°C. In one embodiment, the heat treatment is a two stage process where the dried material is heated to one temperature and held at this temperature before being heated to and held at another temperature. An example of this two stage process is where the dried material is heated to 300°C and held at this temperature for a period of time (e.g. 1 hour) before being heated to 675°C and being held at this temperature for a second period of time (e.g. 1 hour). In an alternative embodiment, the dried material may be heated to a particular temperature (e.g. 700°C) and held at this temperature for a period of time (such as about 1 hour).

The heat treatment is carried out in an atmosphere which inhibits oxidation of the dried material. Preferably, the non-oxidising atmosphere comprises argon or nitrogen.

The process of the present invention may further comprise pre-treating the carbon support before step (a). In this respect, the pre-treatment comprises the steps of:

- (i) contacting the carbon support with a solution of an acid or a base and a surfactant in a solvent, preferably a protic solvent;
- (ii) optionally washing the product of step (i) one or more times; and
- (iii) drying and heat treating the product of step (i) or step (ii) under a non-oxidising atmosphere.

The pre-treatment can help to remove metal ions which may inevitably be present in the carbon support.

The carbon support, solvent, protic solvent, optional washing step, drying and heat treatment are generally as described above.

In some embodiments, it is preferable that the carbon support is contacted with a solution of a base and a surfactant. The base may be an organic or inorganic base. In one embodiment, the inorganic base is an alkali metal carbonate, ammonium carbonate (NH_4CO_3) or tetraalkylammonium carbonate. In another embodiment, the inorganic base is selected from the group consisting of sodium carbonate and potassium carbonate. In another embodiment, the tetraalkylammonium carbonate may be selected from the group consisting of $[\text{Bu}_4\text{N}]_2\text{CO}_3$, $[\text{Bu}_4\text{N}]\text{CO}_3$ and $[\text{Bu}_4\text{N}]\text{CO}_3$.

Where the carbon support is contacted with a solution of an acid and a surfactant, preferably the acid is a non-oxidising acid, such as hydrochloric acid. Oxidising acids may undesirably oxidise the carbon support.

In one embodiment, the surfactant is selected from an anionic, cationic or neutral surfactant. In one embodiment, the surfactant is a cationic surfactant, such as cetyltrimethylammonium bromide (CTAB). In another embodiment, the surfactant is a neutral surfactant, such as oleylamine. In yet another embodiment, the surfactant is an anionic surfactant, such as a surfactant comprising a permanent anion, for example, surfactants comprising one or more sulfonate, phosphate or carboxylate groups. In yet another embodiment, the surfactant is an anionic surfactant comprising a pH dependent anion, such as oleic acid or dodecyl succinic anhydride.

In some embodiments, the base may also act as a surfactant. In this instance, therefore, it may not be necessary to include a surfactant in the reaction mixture beyond the addition of the base. Examples of bases which may also act as a surfactant include but are not limited to CTAB and oleylamine.

In another aspect, the invention provides an electrocatalyst suitable for use in a fuel cell for the generation of hydrogen peroxide comprising an activated transition metal-free carbon support obtainable by the process comprising the steps of:

- (a) contacting a carbon support with a solution of an activating agent in a solvent, preferably a protic solvent, wherein the activating agent comprises at least one amino group;
- (b) optionally washing the product of step (a) one or more times; and
- (c) drying and heat treating the product of step (a) or step (b) under an non-oxidising atmosphere to form the electrocatalyst.

The electrocatalyst and process for its preparation are generally similar to those described above.

The electrocatalysts of the present invention may be used as such or in association with one or more other catalysts or promoters.

The present invention further provides components and a method for the manufacture of hydrogen peroxide. The electrocatalysts may be incorporated into a MEA using conventional technology, such as forming an electrocatalytic ink, for printing onto a PEM membrane or onto a gas diffusion electrode to form a cathode. The MEA may be incorporated into a PEMFC or fuel cell stack. In use, the cathode is supplied with humidified oxygen, and a standard catalysed anode supplied with humidified hydrogen. No external power is required. Operating at temperatures between about 10°C and about 40°C, hydrogen peroxide solution may be withdrawn from the cell at industrially-useful concentrations. Under preferred conditions, and using optimised conditions to reduce oxygen stoichiometry and water, hydrogen peroxide solutions of over 9 wt% have been seen. Furthermore, the cells have been continuously operated in the laboratory for several days without any noticeable loss of performance, indicating good stability.

Indicative cell operating conditions are 40-100 mV and a current of 300 mA/cm². There does not appear to be active hydrogen evolution, suggesting that the risk of explosion during operation may be minimised. Operation relatively close to the hydrogen potential reduces the tendency for corrosion of the cathodic electrocatalyst.

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The hydrogen peroxide-generating fuel cells of the invention permit generation of hydrogen peroxide locally, at point of use. Potentially, this may even be generated in small industry or domestic environments, such as for swimming pools, laundry and cleaning etc. It is conceivable that the hydrogen peroxide may be combined with other materials, such as acetic acid, or with other biocides, to be an effective combined biocide. This may be useful in the control of biofilms or algal growth. The hydrogen peroxide may also be used as a reagent in chemical processes.

In order that the invention may be more fully understood the following non-limiting Examples are provided by way of illustration only and with reference to the accompanying Figures in which:

15

Figure 1a shows the ring/disk currents as a function of potential for various catalysts prepared according to Examples 1, 2a-c, 3a-b and 4.

Figure 1b shows the efficiency of the electrochemical formation of peroxide as a function of potential for the catalysts in Figure 1a.

20

Figure 1c shows the pressure rise due to chemical decomposition of hydrogen peroxide in 0.1M sulphuric acid in the presence of the electrocatalysts prepared according to Examples 1, 2a-c, 3a-b and 4.

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Figure 2a shows a direct comparison for the ring/disk electrode behaviour for the Co and metal-free catalysts prepared according to Examples 6 and 8b. Figure 2b shows the associated peroxide production efficiency, and Figure 2c the chemical decomposition behaviour.

Figure 3a shows a direct comparison for the ring/disk electrode behaviour for the Co and metal-free catalysts prepared according to Examples 7 and 8a. Figure 3b shows the associated peroxide production efficiency, and Figure 3c the chemical decomposition behaviour.

30

Figure 4a shows the current-voltage polarisation plot for a 49cm² single cell for the metal-free catalyst prepared according to Example 7.

35

Figure 4b shows the production of hydrogen peroxide as a function of time over four days for the catalyst made by Example 7 when used in a 49cm² single cell (conditions as per Figure 4a).

Figure 5 shows shows XPS data for an electrocatalyst prepared according to Example 1.

40

Figure 6 shows the results of Example 14, demonstrating stable production of hydrogen peroxide in a fuel cell.

Examples

Chemicals

Triethylenetetramine (TETA) 97%, ortho-phenylenediamine 98%, and hydrogen peroxide 35%, were purchased from Alfa Aesar. Perchloric acid, double distilled, 70%, was obtained from Veritas®. Argon, nitrogen and hydrogen from Air Liquide. MilliQ water (Millipore Inc.) was used to prepare dilute acid solutions as appropriate.

Electrocatalyst characterisation

All potentials are referred to the reversible hydrogen electrode (RHE). A rotating ring disc electrode (RRDE) from Pine Company (Grove City, PA, USA) with a glassy carbon (GC)/Pt disc-ring electrode of 0.247 cm² disc area was employed using a Modulated Speed Rotator (MSR), which includes a speed controller. The ring potential was set at 1.2 V for the quantitative detection of the peroxide produced at the ring. A collection efficiency of 0.4 was determined from measurements with hexacyanoferrate (III) reduction. The electrochemical experiments were performed in a three compartment cell with controlled atmosphere and room temperature (293 K (20°C) for all the experiments). The applied potential was controlled with an Autolab potentiostat/galvanostat PGSTAT 30 (Metrohm, USA). The reference electrode used was H₂ purged Pd/C electrode acting as an RHE. A Pt coil served as the counter electrode, which was separated from the working electrode by a fine glass frit. The electrolyte in all the measurements was aqueous 0.1 M HClO₄ saturated with N₂ or O₂ as required. The sweep rate in all ORR experiments was 20 mVs⁻¹. The electrodes were prepared by sonicating 5mg in 5mls deionised water followed by micropipetting 5 microlitres of the suspension onto the glassy carbon disk electrode and allowing it to dry under an infra-red lamp for 1 minute.

The chemical decomposition kinetics for hydrogen peroxide in the presence of catalysts at open-circuit were investigated by recording the increase in pressure with time of a closed vessel at room temperature when a known amount of hydrogen peroxide was injected via a rubber septum into a magnetically stirred slurry of the test catalyst suspended in 0.1M sulfuric acid. The pressure sensor was a Baumer E613 pressure sensor from RS Components.

Gas diffusion electrodes for testing in a 49cm² hydrogen/oxygen single-cell were prepared by screen-printing of the catalyst-ink onto Toray carbon-fibre paper using standard procedures widely used in the PEM fuel cell industry. Current-voltage plots were obtained by operating the single-cell with 1700mbar hydrogen and oxygen gases fully humidified at 80°C.

Example 1

Preparation of an activated transition-metal free electrocatalyst without pre-treatment of the carbon support

o-Phenylenediamine (0.89g) and water (50 mL) were added to a 100 mL beaker. The beaker was heated to promote the dissolution of the o-phenylenediamine. The reaction mixture was then cooled to room temperature and added to a 1000 mL beaker.

- 5 Commercially available carbon BP2000 (10 g) was added to the previous mixture to form a slurry. 300 mL of water was added to allow better stirring. Stirring was continued until a homogeneous mixture was formed. The mixture was allowed to rest overnight.

The following day, the mixture was washed with deionised water (300 mL, repeated twice) and the
10 preparation dried in an oven at 80°C overnight.

The dried material (11.2 g) was fired in a furnace under an argon atmosphere as follows:

- a) Ramp temperature 10°C/min to 300°C, then 60 min hold at this temperature;
- b) Ramp temperature 10°C/min to 675°C, hold for 60 min at this temperature.

- 15 After cooling, the resulting catalyst was collected (10.5 g).

Example 2

Preparation of activated transition-metal free electrocatalysts without pre-treatment of the carbon support

20 Electrocatalysts were prepared following the procedures described in Example 1 replacing BP2000 with the following carbons:

- a) ECJ300;
- b) ECJ300 graphitised at 2500°C; and
- c) Vulcan XC-72R.

25

Example 3

Preparation of activated transition-metal free electrocatalysts without pre-treatment of the carbon support

Electrocatalysts were prepared using the following amines:

- 30 a) Triethylenediamine (TETA); and
- b) Diaminooctane.

The procedures for preparing the electrocatalysts were as described in Example 1 except that o-phenylenediamine was replaced with TETA or diaminooctane. The TETA example was also heated
35 treated at 700°C instead of 675°C.

Example 4 (Comparative)

Preparation of 2wt% Co/oPD/BP2000 electrocatalyst

40 CoCl₂ (0.39g; 1 molar equivalent), o-phenylenediamine(0.89g; 8 molar equivalents) and water (50 mL) were added to a beaker. The beaker was heated to promote the dissolution of the CoCl₂ and o-phenylenediamine. The reaction mixture was then cooled to room temperature and added to a 1000 mL beaker.

Commercially available carbon BP2000 (10 g) was added to the previous mixture to form a slurry. 300 mL of water was added to allow better stirring. Stirring was continued until a homogeneous mixture was formed. The mixture was allowed to rest overnight.

5

The following day, the mixture was washed with deionised water (300 mL, repeated twice) and the preparation dried in an oven at 80°C overnight.

The dried material was fired in a furnace under an argon atmosphere as follows:

- 10 a) Ramp temperature 10°C/min to 300°C, then 60 min hold at this temperature;
 b) Ramp temperature 10°C/min to 675°C, hold for 60 min at this temperature.

After cooling, the resulting catalyst was collected.

Example 5

Pre-treatment of the carbon support

15 Into a 100 mL beaker NaCO₃ (1.145 g), CTAB (cetyltrimethylammonium bromide) (4.011g) and water (14 mL) were added at room temperature. The solution was agitated for 16 hours at 80°C. The reaction was then cooled to room temperature and added to a 400 mL beaker.

- 20 Commercially available carbon BP2000 (8g) was added to the previous mixture and a slurry formed. 300 mL of water were added to allow better stirring. Stirring was continued until a homogeneous mixture was formed. The mixture was allowed to rest overnight.

- 25 The following day, the solution was washed with deionised water (300 mL, repeated twice). The preparation was dried in an oven at 80°C. The dried material was fired at 300 °C under nitrogen or argon and cooled.

Example 6

Preparation of an activated transition-metal free electrocatalysts using a pre-treated carbon support

- 30 Into a 50 mL beaker was added 0.55 g of o-phenylenediamine with the minimum amount of hot water (7 mL) and the mixture stirred. The beaker was heated to promote the dissolution of the amine. The solution was then added to a beaker containing 3g of the pre-treated carbon support prepared according to Example 5 and stirred until a homogeneous mixture was formed. The preparation was
35 dried in an oven at 80°C overnight.

The dried material was fired in a furnace under an argon atmosphere as follows:

- a) Ramp temperature 10°C/min to 300°C, then 60 min hold at this temperature; then
b) Ramp temperature 10°C/min to 675°C, hold for 60 min at this temperature.

40

After cooling, the fired catalyst was collected.

Example 7

Preparation of an activated transition-metal free electrocatalysts using a pre-treated carbon support

Into a 100 mL beaker was added 3.31 g of o-phenylenediamine with the minimum amount of hot water (40 mL) and the mixture stirred. The beaker was heated to promote the dissolution of the ligand. The solution was then added to a beaker containing 3g of the pre-treated carbon support prepared according to Example 5 and stirred until a homogeneous mixture was formed. The preparation was dried in an oven at 80°C overnight.

The dried material was fired in a furnace under an argon atmosphere as follows:

- a) Ramp temperature 10°C/min to 300°C, then 60 min hold at this temperature; then
- b) Ramp temperature 10°C/min to 675°C, hold for 60 min at this temperature.

After cooling, the fired catalyst was collected.

Example 8 (Comparative)

Preparation of 2wt% Co/oPD/BP2000

Two samples of 2wt% Co/oPD/BP2000 electrocatalysts were prepared according to Example 4 changing the quantities of o-phenylenediamine such that:

- a) 30 molar equivalents of o-phenylenediamine were used; and
- b) 5 molar equivalents of o-phenylenediamine were used.

Example 9

Electrochemical and chemical decomposition studies

Electrochemical and chemical decomposition studies were carried out on the electrocatalysts prepared according to Examples 1, 2a-c, Examples 3a-b and 4 (see Figures 1a-c).

Figure 1a illustrates the ring/disk currents as a function of potential for various catalysts. Currents in the positive Y-axis domain represent ring currents for peroxide oxidation, and currents in the negative Y-axis domain correspond to the electrochemical reduction of oxygen to form hydrogen peroxide and also includes any further reduction processes e.g. peroxide to water.

Figure 1b shows the efficiency of the electrochemical formation of peroxide as a function of potential for the catalysts in Fig. 1a. For the cobalt-containing catalyst the range of electrochemical potentials over which peroxide can be produced is larger than for the metal-free catalysts. However, the efficiency of peroxide production for all the catalysts is broadly similar between 0.2 and 0.0V.

Figure 1c shows the pressure rise due to chemical decomposition of hydrogen peroxide in 0.1M sulphuric acid in the presence of various catalysts. Only the Co-containing catalyst shows significant reactivity for peroxide decomposition. This shows that the absence of metal ions in the catalyst results in very low chemical decomposition of the peroxide.

Example 10

Electrochemical and chemical decomposition studies

Electrochemical and chemical decomposition studies were carried out on the electrocatalysts prepared according to Examples 6 and 8b (see Figures 2a-c).

Figure 2a illustrates a direct comparison for the ring/disk electrode behaviour for the Co and metal-free catalysts made with o-phenylene diamine activator (5 molar excess activator with respect to metal), Figure 2b shows the associated peroxide production efficiency, and Figure 2c the chemical decomposition behaviour.

Figures 2a-b show that whilst the Co-containing catalyst appears to have better electro-catalytic properties (i.e. there is more disk and ring currents at higher potentials compared to the metal-free system), the catalysis of the chemical decomposition of hydrogen peroxide, which is undesirable, is greatly promoted by the metal-containing catalyst (Figure 2c).

Example 11

Electrochemical and chemical decomposition studies

Electrochemical and chemical decomposition studies were carried out on the electrocatalysts prepared according to Examples 7 and 8a (see Figures 3a-c).

Figure 3a illustrates a direct comparison for the ring/disk electrode behaviour for the Co and metal-free catalysts made with o-phenylene diamine activator (30 molar excess activator with respect to metal), Figure 3b shows the associated peroxide production efficiency, and Figure 3c the chemical decomposition behaviour.

Figures 3a-b show that whilst the Co-containing catalyst appears to have better electro-catalytic properties (i.e. there is more disk and ring currents at higher potentials compared to the metal-free system), the catalysis of the chemical decomposition of hydrogen peroxide, which is highly undesirable, is greatly promoted by the metal-containing catalyst (Figure 3c).

Example 12

The electrocatalyst prepared according to Example 7 was tested in a PMCFC single cell and the results illustrated in Figures 4a and 4b:

Figure 4a shows the current-voltage polarisation plot for a 49cm² single cell for the metal-free catalyst prepared according to Example 7. The open-circuit voltage is close to 0.8V and drops exponentially as current is progressively drawn from the cell as expected for this type of reaction.

Figure 4b shows the production of hydrogen peroxide as a function of time over four days for the catalyst made by Example 7 when used in a 49cm² single cell (conditions as per Figure 4a). This shows that the production of hydrogen peroxide requires some hours to reach steady-state due to the relatively large dead-space between the catalyst layer and the collection point of liquid from the cell.

Example 13

XPS Data

Figure 5 shows XPS data for an electrocatalyst prepared according to Example 1. These data demonstrate that nitrogen containing species are present at the surface of the activated carbon electrocatalyst. The major signal (~399 eV) indicates a specific amine-like carbon-nitrogen species.

The broader signal centered on ~400 eV is typical of random amine-like nitrogen species on carbon materials.

Example 14

Electrocatalyst according to the present invention was tested over an extended period of time in a PEM fuel cell. The cell had an active area of 49cm². The current density was fixed at 100mA/cm² and the cathode was fed with oxygen at 1.7barg (290ml/min flow) and the anode with hydrogen at 1.7barg (60ml/min flow). Reactant gas was humidified with water vapour from an external reservoir held at 60°C. The cell temperature was maintained at approximately 25°C. The membrane electrode assembly was constructed using Nafion®115 membrane, with a 30wt% Pt on carbon anode layered on Toray H60 carbon paper, and with a cathode containing 2.8mg/cm² of total catalyst and support on a Toray H60 carbon paper.

The results are shown in Figure 6. These results demonstrate consistent production for approximately 11% hydrogen peroxide over an extended running period of two weeks. This illustrates that the electrocatalyst according to the present invention is suitable to provide steady production of hydrogen peroxide over an extended time period.

Claims

1. An electrocatalyst suitable for use in a fuel cell for the generation of hydrogen peroxide
5 comprising an activated transition metal-free carbon support.
2. An electrocatalyst according to claim 1 wherein the activated transition metal-free carbon support comprises a nitrogen-containing layer formed on a surface thereof.
- 10 3. An electrocatalyst according to claim 1 or claim 2, wherein the carbon support has a surface area of from about 10 m²/g to about 2000 m²/g.
4. An electrocatalyst according to any one of claims 1 to 3, wherein the carbon support is selected from the group consisting of BP2000, ECJ300, ECJ300 graphitised at 2500°C and Vulcan XC-
15 72R.
5. A process for the preparation of the electrocatalyst as defined any one of claims 1 to 4, comprising the steps of:
 - 20 (a) contacting a carbon support with a solution of an activating agent in a solvent, wherein the activating agent comprises at least one nitrogen-containing functional group;
 - (b) optionally washing the product of step (a) one or more times; and
 - (c) drying and heat treating the product of step (a) or step (b) under an non-oxidising atmosphere to form the electrocatalyst.
- 25 6. A process according to claim 5 wherein the nitrogen-containing functional group is selected from amino, nitro and amino oxide.
7. A process according to claim 5 or claim 6, wherein the activating agent is selected from the group consisting of an arylamine, alkylamine and heteroarylamine, wherein the arylamine, alkylamine and heteroarylamine independently have one or more amino groups, and wherein
30 the arylamine, alkylamine and heteroarylamine are independently substituted or unsubstituted.
8. A process according to claim 7, wherein the activating agent is selected from the group consisting of aniline, phenylenediamine, triethylenetetramine and diaminooctane.
- 35 9. A process according to any one of claims 5 to 8, wherein the carbon support is pre-treated before step (a), wherein the pre-treatment comprises the steps of:
 - (i) contacting the carbon support with a solution of base and a surfactant in a solvent;
 - (ii) optionally washing the product of step (i) one or more times; and

(iii) drying and heat treating the product of step (i) or step (ii) under a non-oxidising atmosphere.

10. A process according to claim 9, wherein the base is an organic or inorganic base.

5

11. A process according to claim 10, wherein the inorganic base is selected from the group consisting of an alkali metal carbonate, ammonium carbonate and tetraalkylammonium carbonate.

10 12. A process according to any one of claims 9 to 11, wherein the surfactant is an anionic, cationic or neutral surfactant.

13. A process according to claim 12, wherein the cationic surfactant is cetyltrimethylammonium bromide.

15

14. A method for the generation of hydrogen peroxide comprising the use of an electrocatalyst according to any one of claims 1 to 4, or as prepared according to any one of claims 5 to 13, in a fuel cell.

20 15. A fuel cell comprising an electrocatalyst according to any one of claims 1 to 4, or as prepared according to any one of claims 5 to 13.

16. A sanitising device comprising a fuel cell according to claim 15.

25 17. Use of a fuel cell according to claim 15 or sanitising device according to claim 16 for the generation of hydrogen peroxide.

18. A method for the manufacture of an electrode for a fuel cell for the production of hydrogen peroxide, the method comprising preparing an electrocatalyst by a method according to any one of claims 5 to 13, and preparing an electrode incorporating said electrocatalyst.

30

19. A method for the manufacture of a fuel cell, the method comprising preparing an electrode by a method according to claim 18, and incorporating the electrode into a fuel cell.

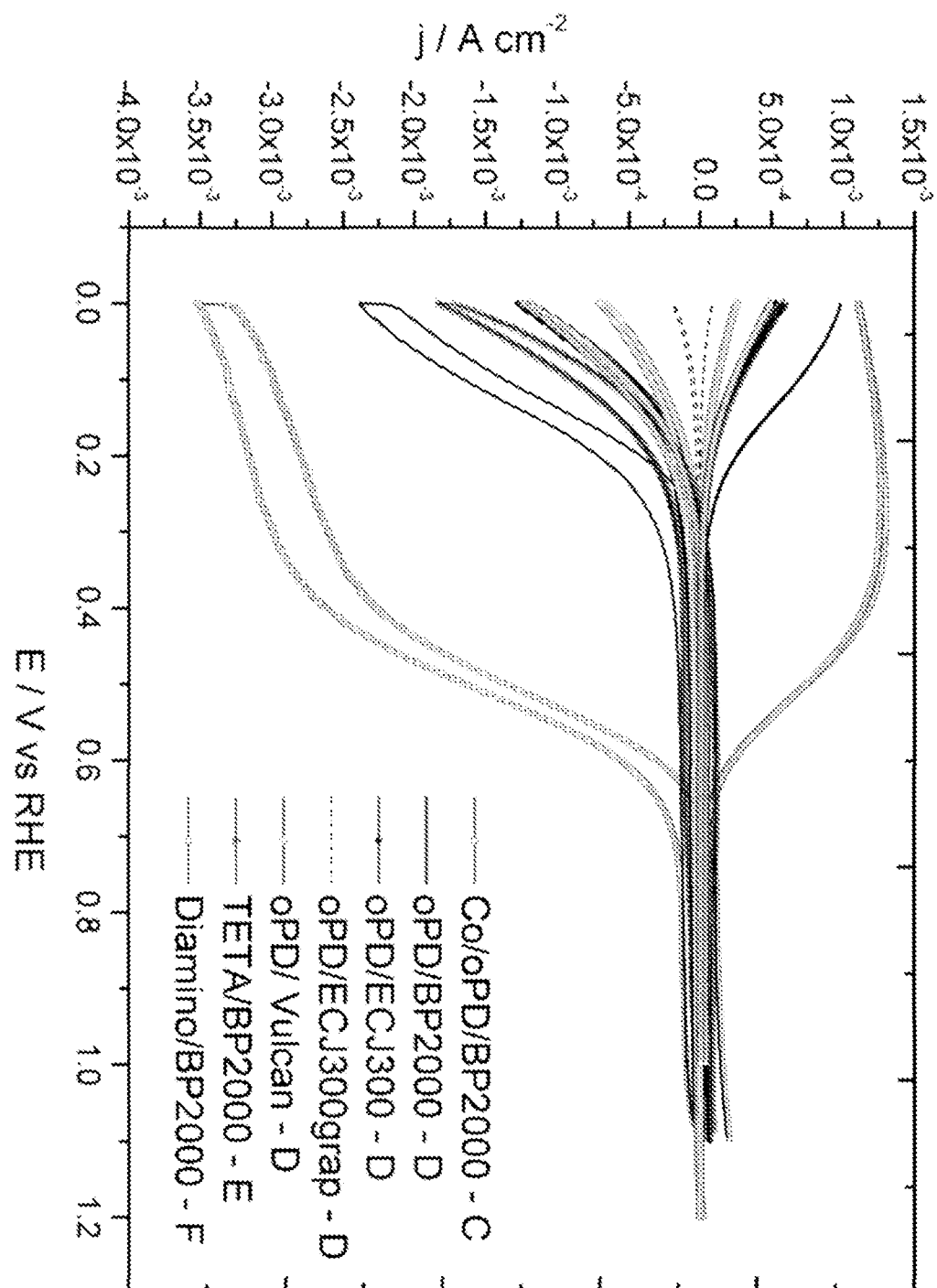


Figure 1a

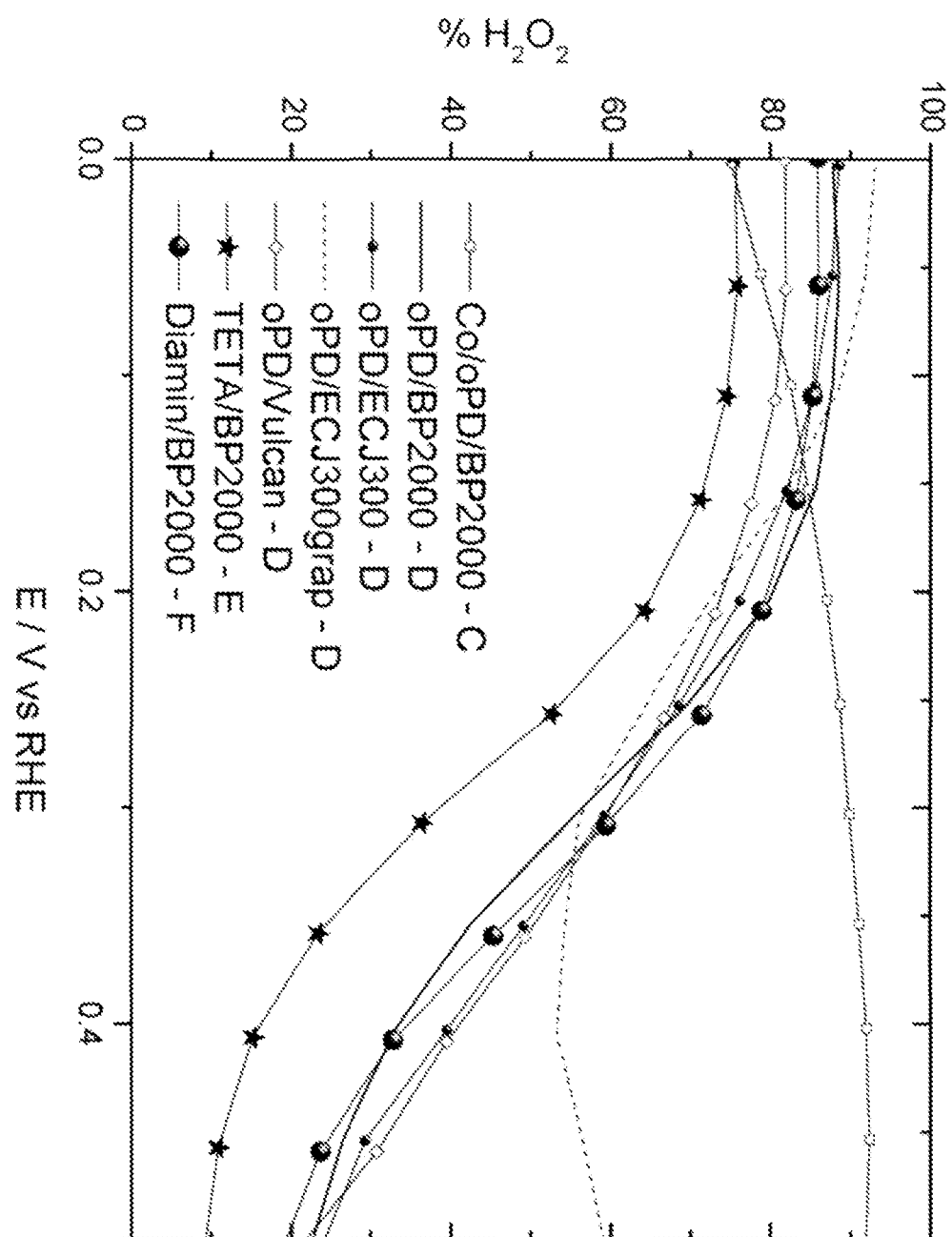


Figure 1b

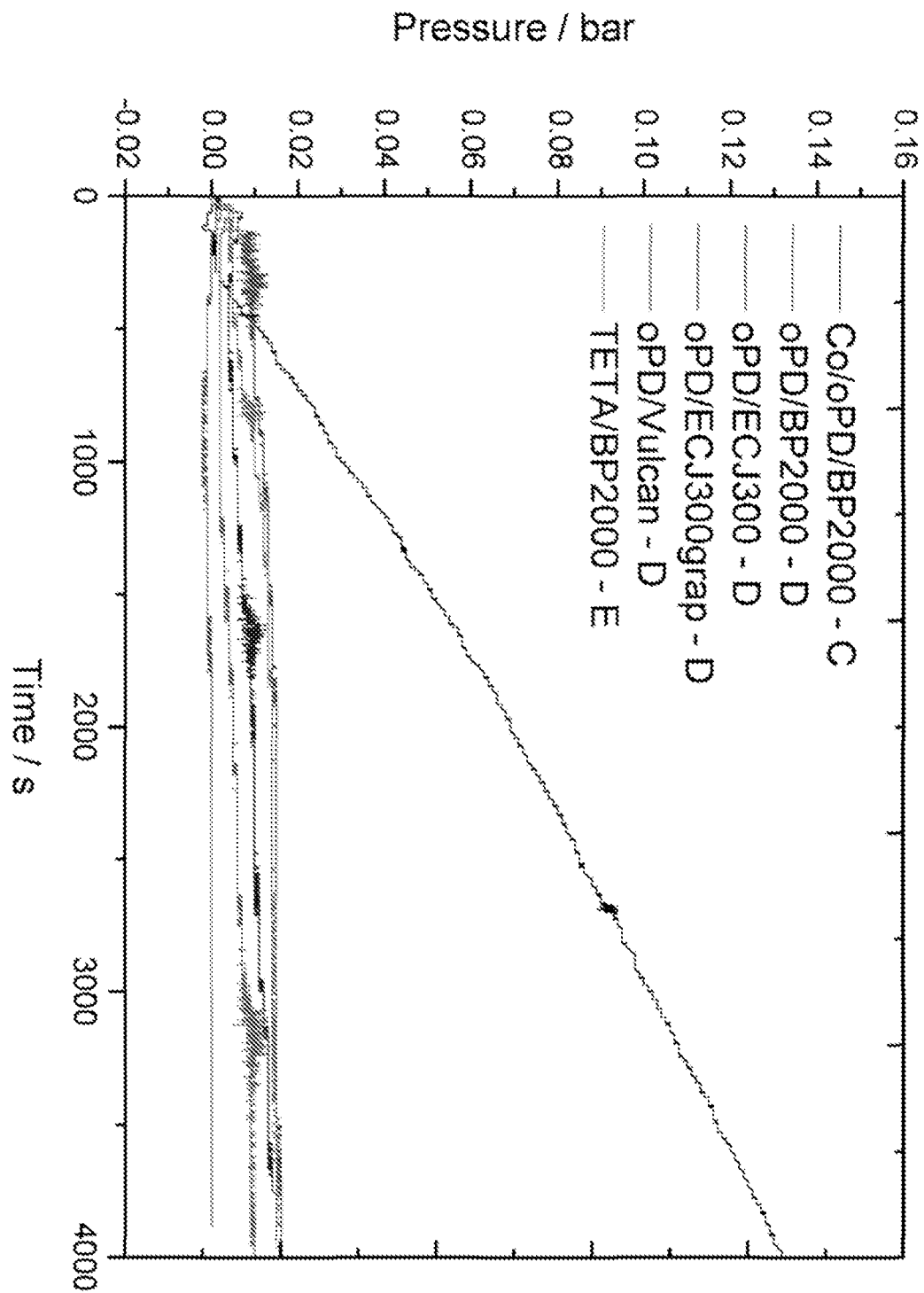


Figure 1c

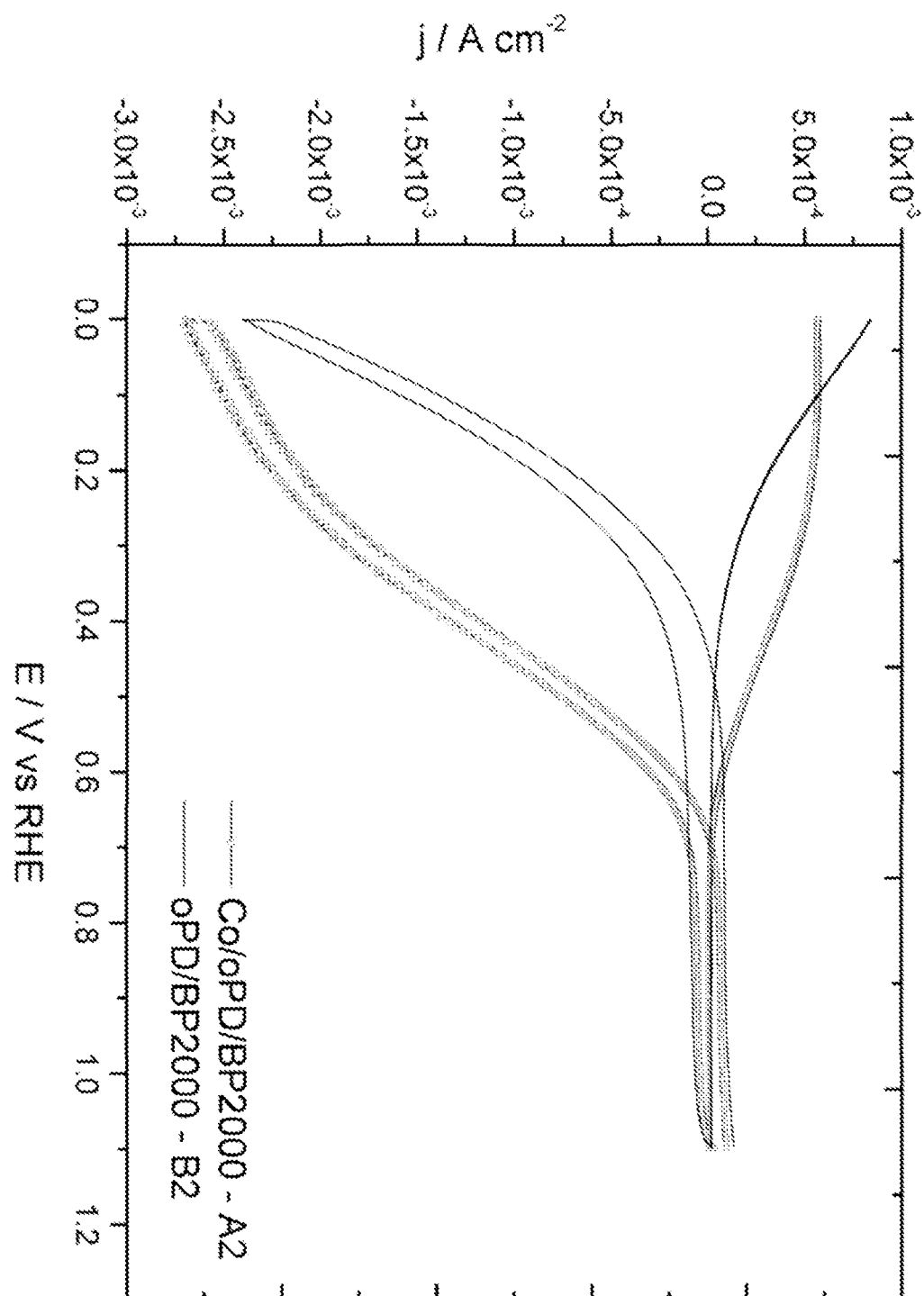


Figure 2a

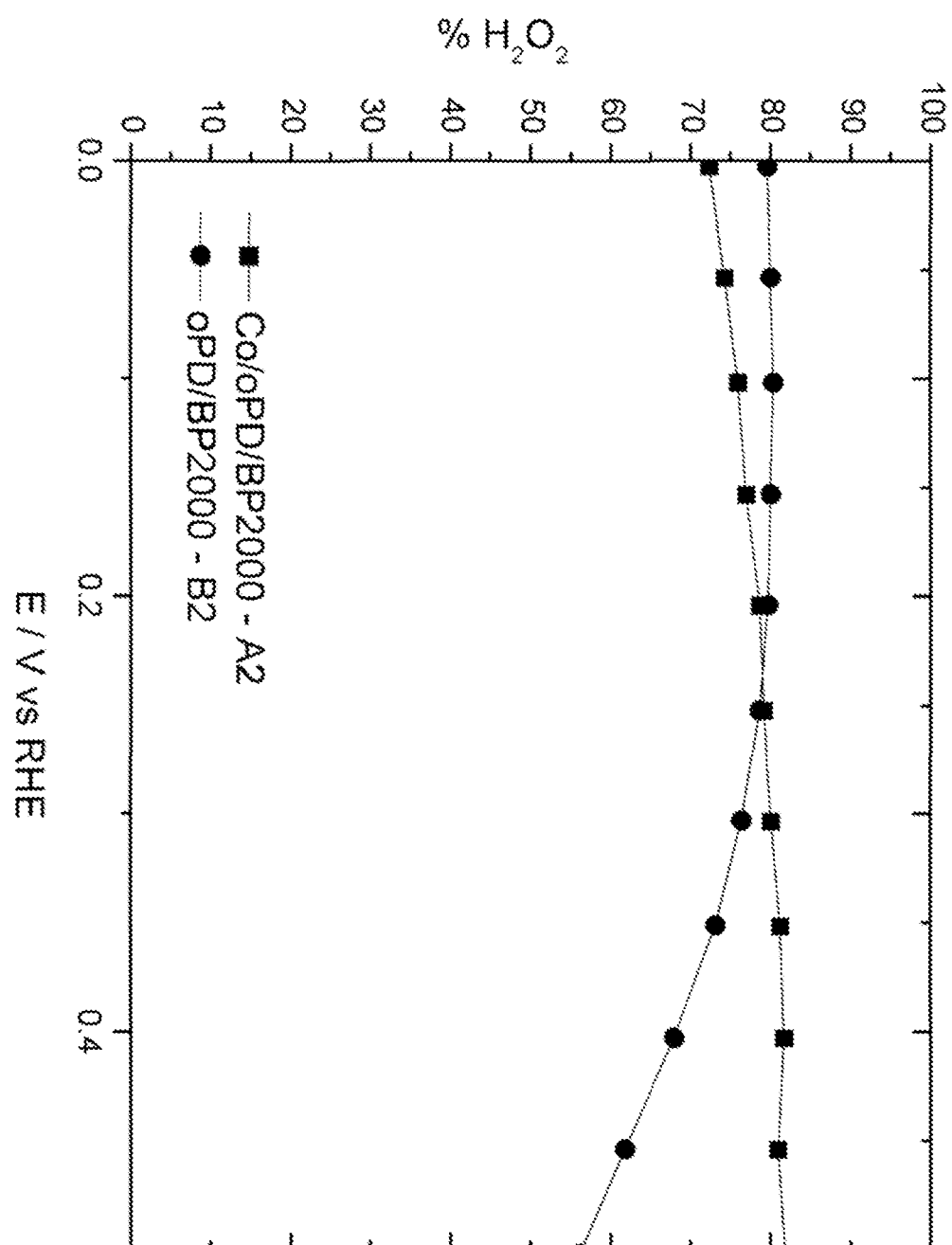


Figure 2b

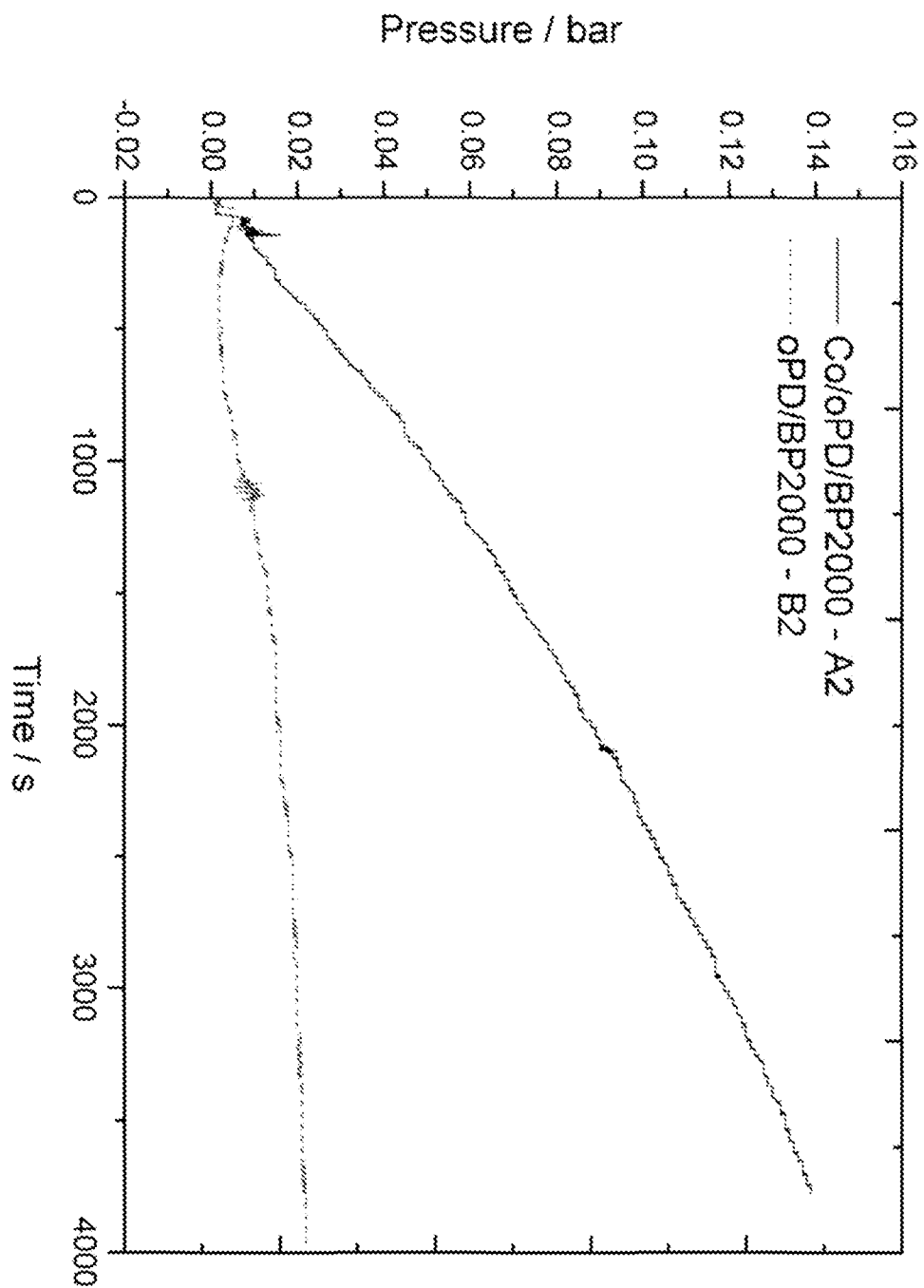


Figure 2c

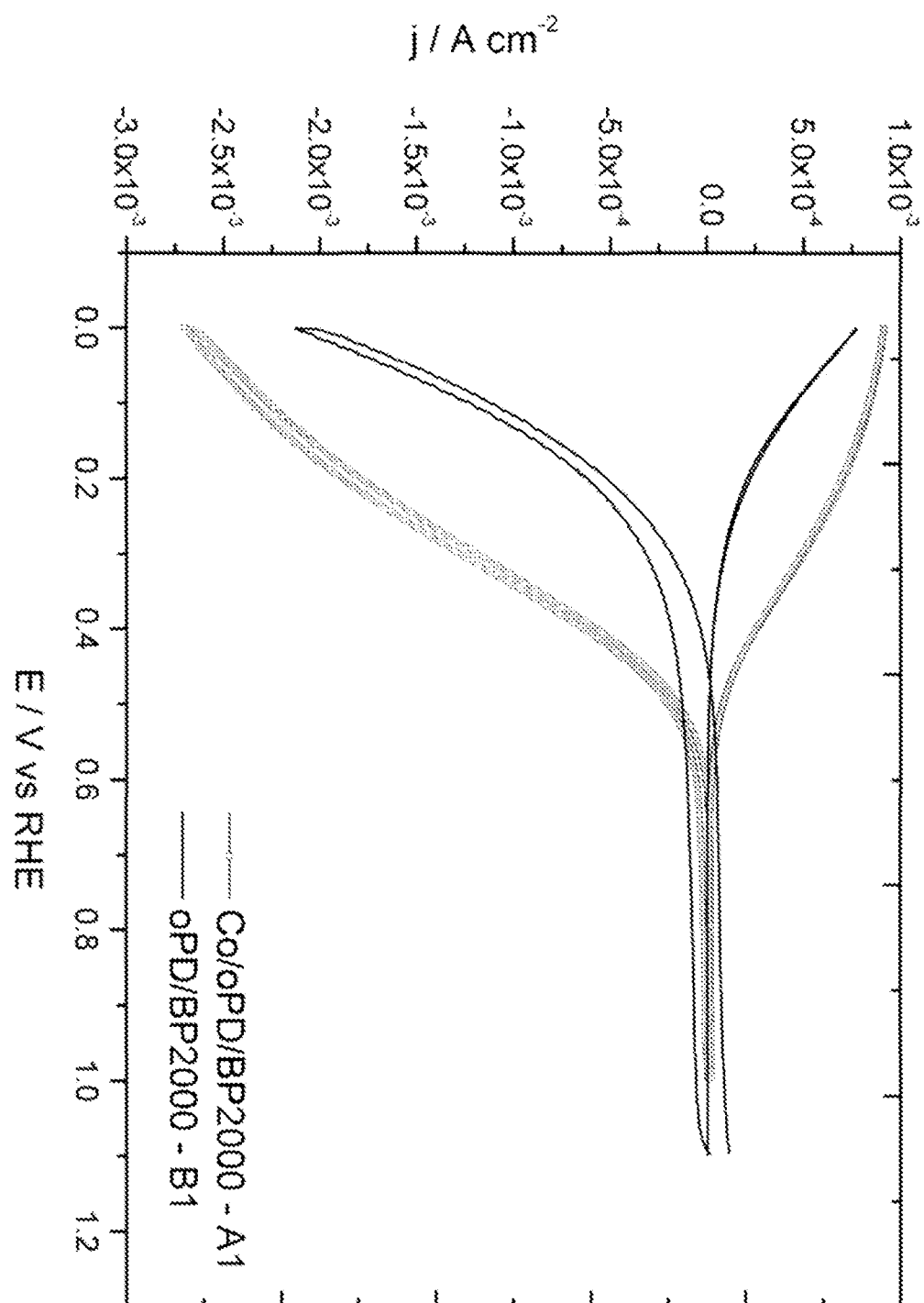


Figure 3a

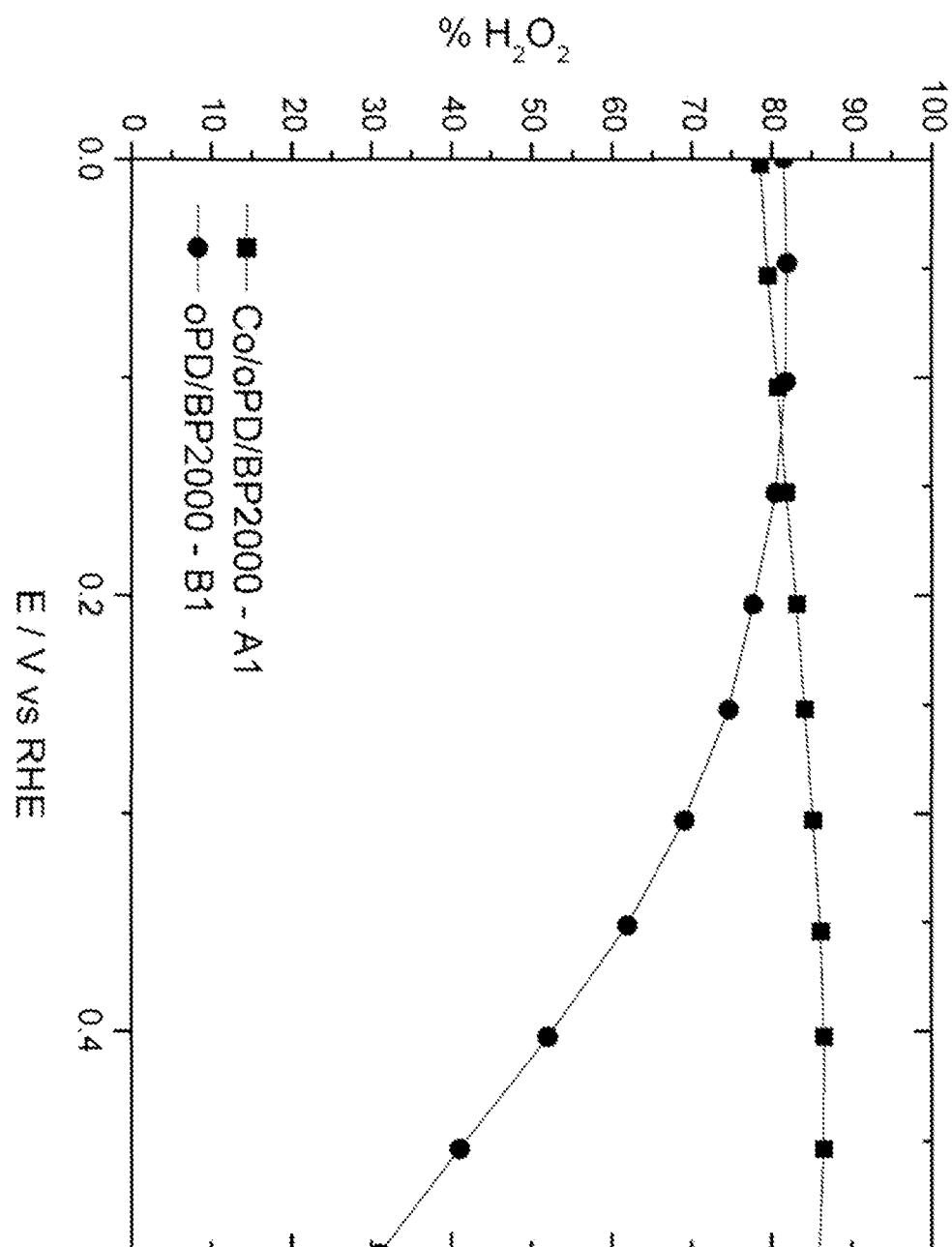


Figure 3b

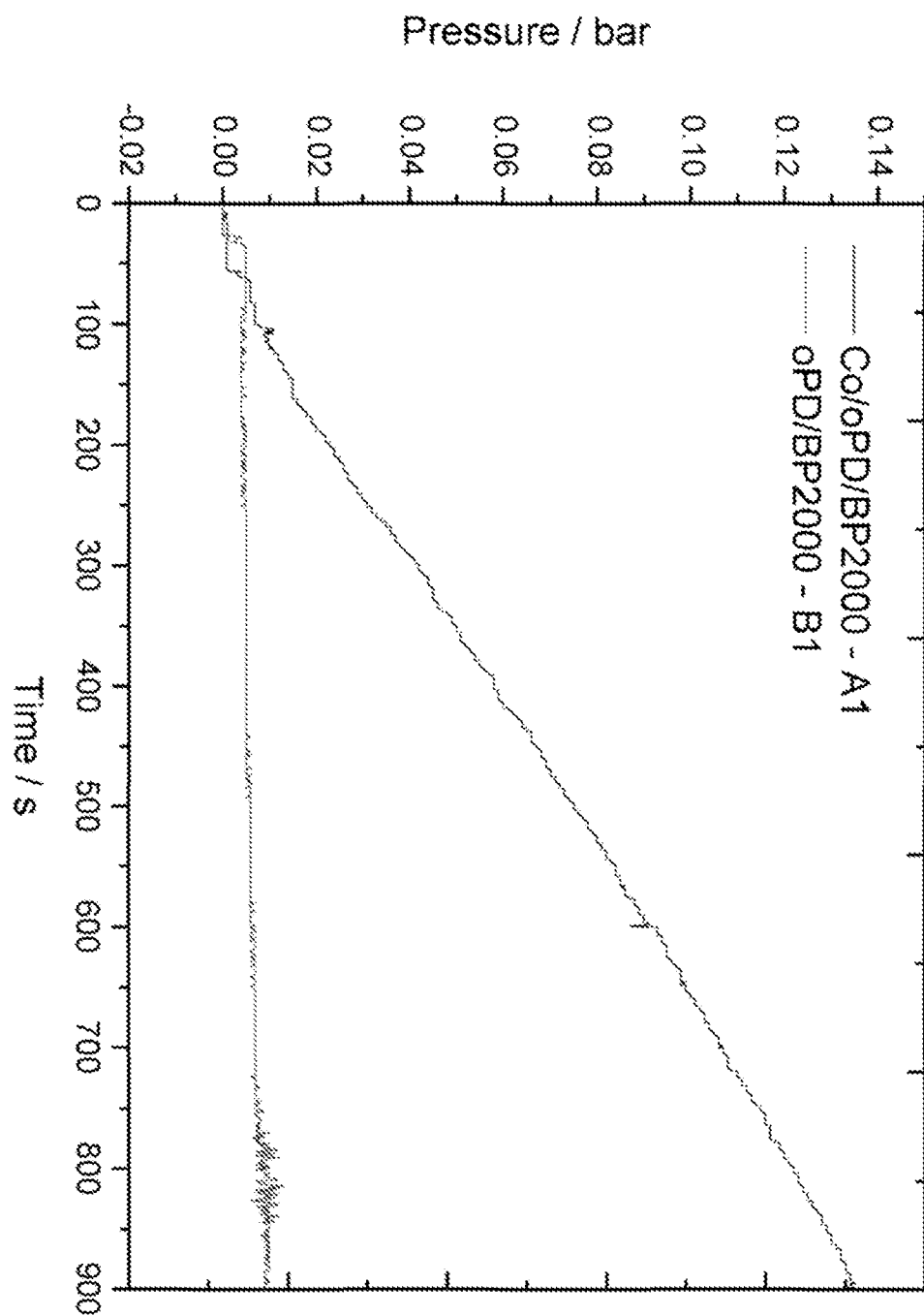


Figure 3c

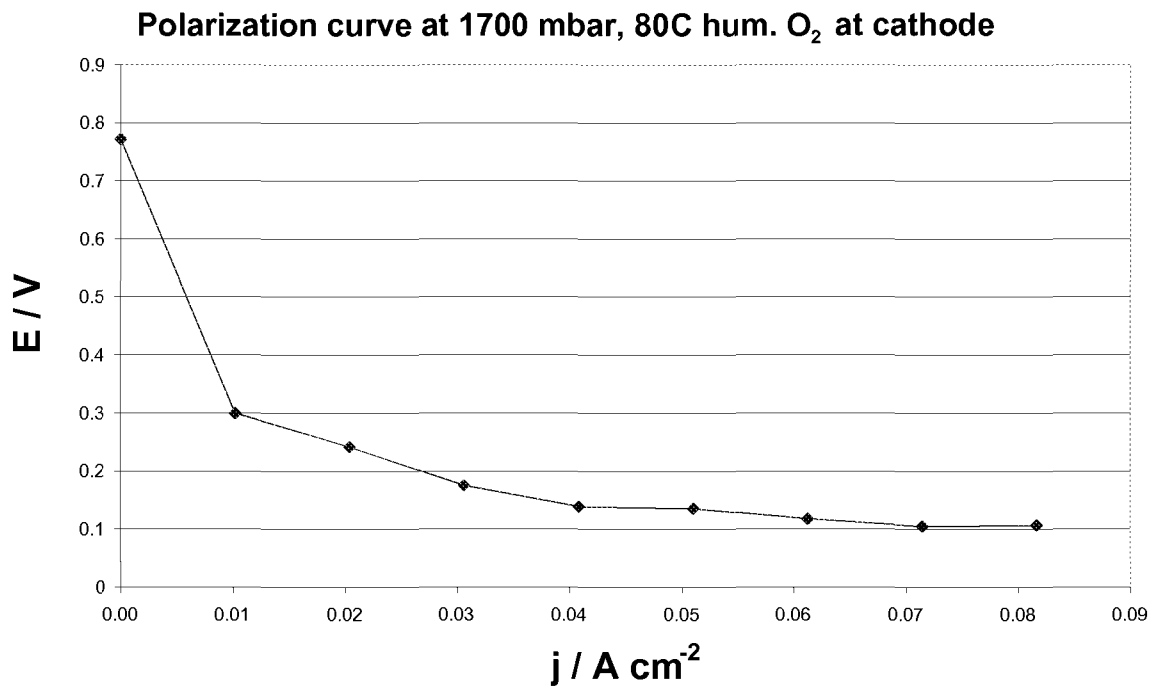


Figure 4a

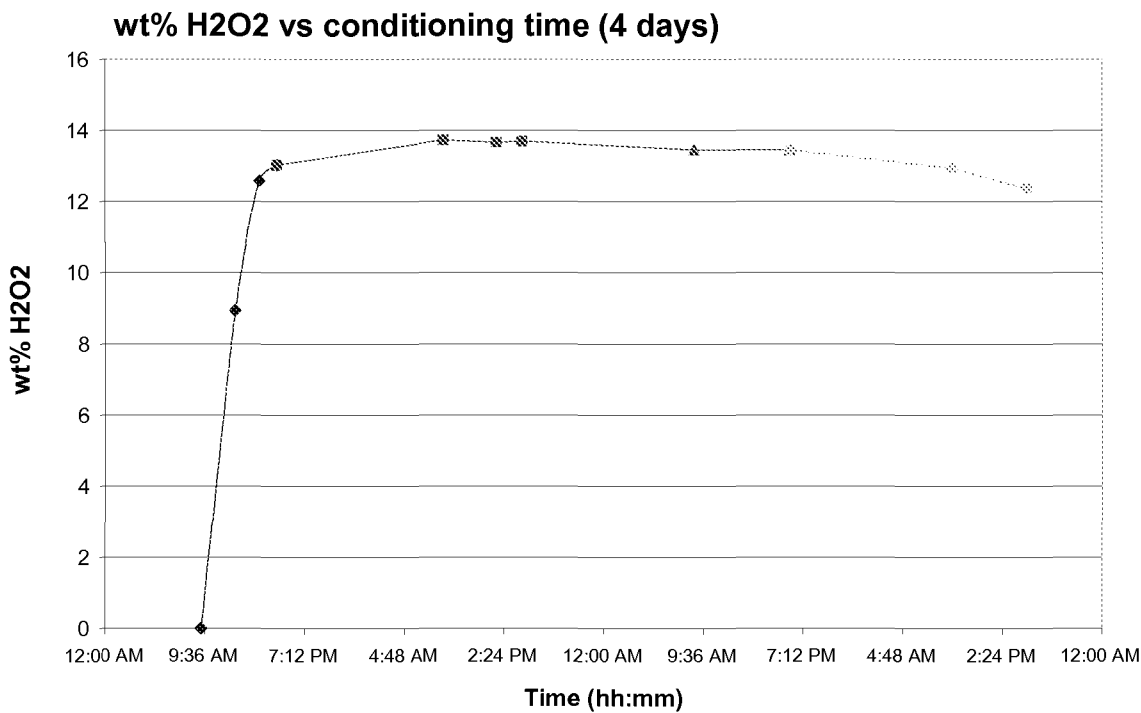


Figure 4b

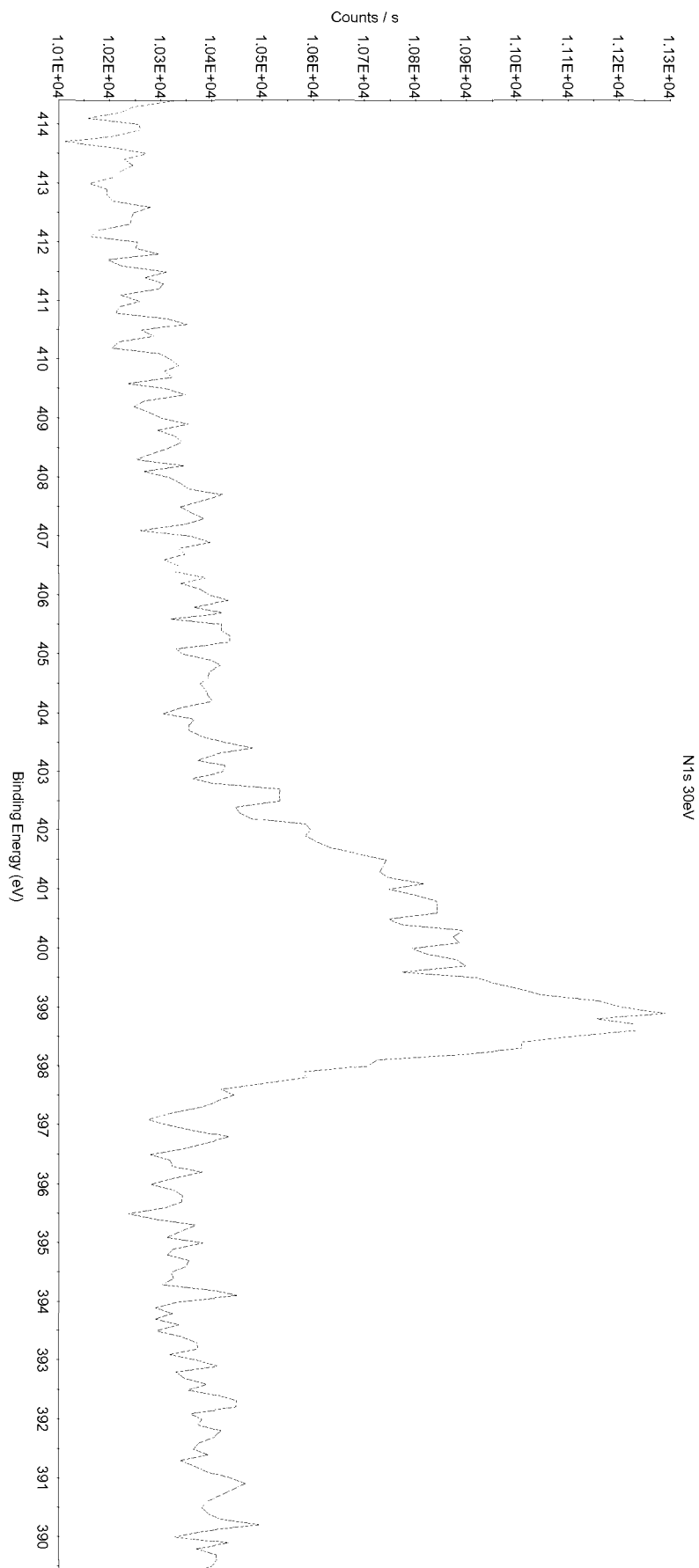
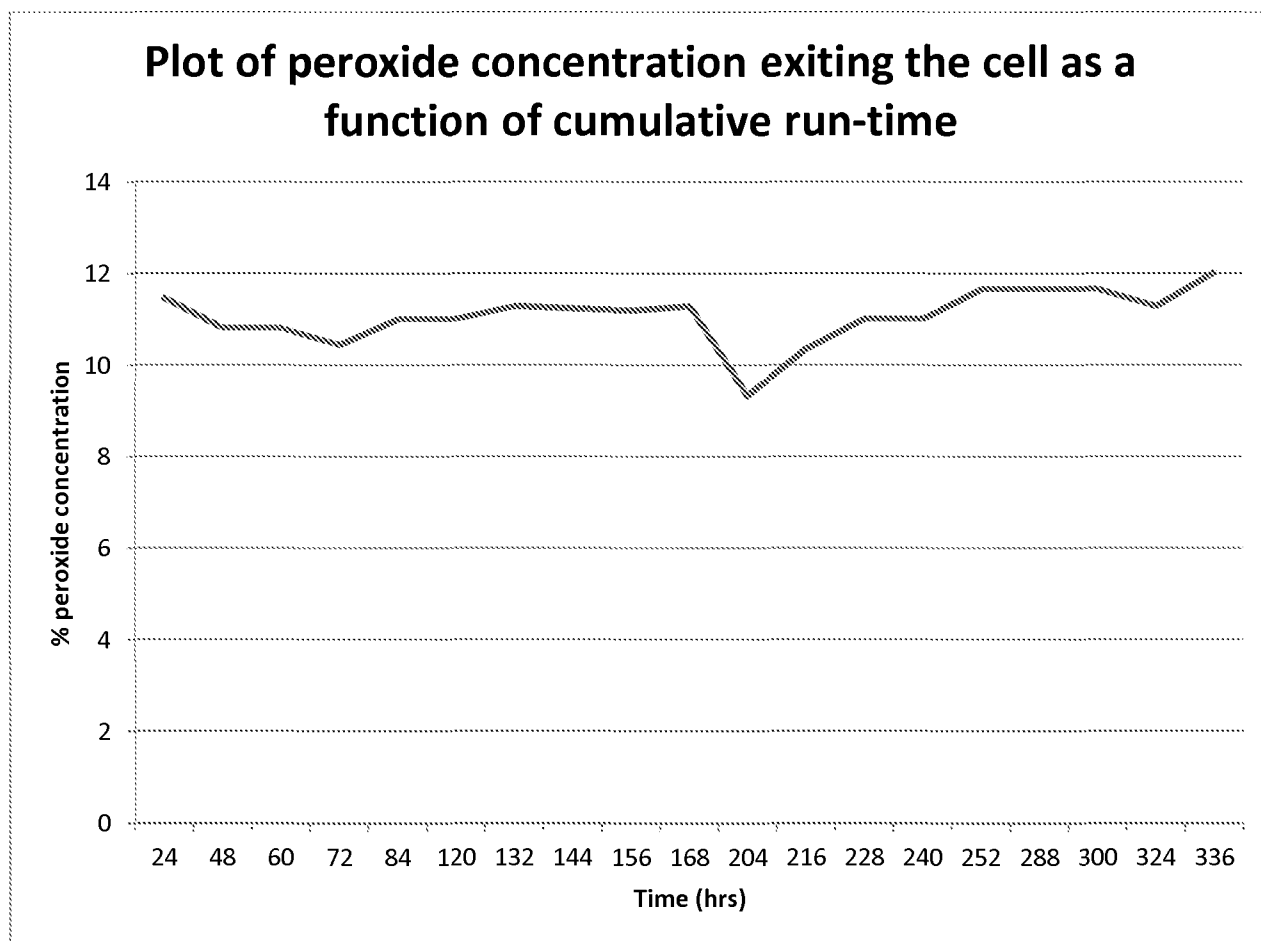


Figure 5

**Figure 6**

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2012/052316

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M4/96 H01M4/86 H01M4/88
ADD.

According to International Patent Classification (IPC) or 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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2008/161183 A1 (POPOV BRANKO N [US] ET AL) 3 July 2008 (2008-07-03)	1-6, 9-15, 17-19
Y	abstract paragraph [0008] paragraph [0014] paragraph [0046] paragraph [0062] ----- -/--	7,8



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

23 November 2012

Date of mailing of the international search report

03/12/2012

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2012/052316

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	K. GONG ET AL: "Nitrogen-Doped Carbon Nanotube Arrays with High Electrocatalytic Activity for Oxygen Reduction", SCIENCE, vol. 323, no. 5915, 6 February 2009 (2009-02-06), pages 760-764, XP055045276, ISSN: 0036-8075, DOI: 10.1126/science.1168049 abstract -----	1,2,14, 15,17
X	US 3 856 640 A (HALFAR K ET AL) 24 December 1974 (1974-12-24) abstract column 5, line 4 - line 15 -----	1,3, 14-17
Y	US 2010/048380 A1 (CALABRESE BARTON SCOTT A [US] ET AL) 25 February 2010 (2010-02-25) paragraph [0051] - paragraph [0053] -----	7,8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2012/052316

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US 3856640	A	24-12-1974	NONE
US 2010048380	A1	25-02-2010	NONE