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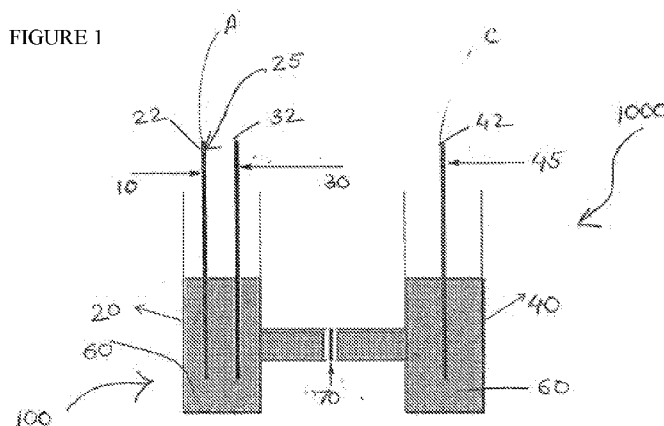
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(54) **Title:** CARBON ELECTRODES

FIGURE 1



(57) **Abstract:** A method of electrolyzing water is described comprising the steps of preparing a carbon electrode by treating a carbon material with one or more ionic liquids so as to functionalise the surface of the carbon material with ions from the ionic liquid. The method also includes the step of electrolyzing water with the carbon electrode. Claimed ionic liquids have a A[pka] in the range of from about 10 to about 20, preferred anions being selected from the group consisting of: RS03⁻ or RCOO⁻, where R is an alkyl or a substituted alkyl group; (CF₃S03)⁻; (R-CF₂CF₂S03)⁻; (CF₃S02)N⁺; (CF₃S02)3C\ CHF₂CF₂S03⁻; (CH₃CH₂S04)⁻, and/or mixtures thereof, while cations including a positively charged nitrogen atom such as a substituted imidazolium are preferred. Fig. 1 shows a typical apparatus for functionalising carbon with an ionic liquid. Carbon in the form of a carbon allotrope, graphite (10), is electrochemically-treated in an electrochemical cell (100). The electrochemical cell (100) includes two cell compartments, a first electrochemical cell compartment (20) and a second electrochemical cell compartment (40). The first compartment (20) and the second compartment (40) are separated by glass frit (70). The electrochemical cell includes a working electrode assembly (25) that is contained in the first compartment (20). The working electrode assembly (25) includes a working electrode (22). Graphite (10) forms at least a part of the working electrode (22). A counter electrode assembly (45) is contained in the second compartment (40). A platinum wire (46) forms a counter electrode (42) in the counter electrode (15) assembly (45). A reference electrode assembly (30) with a reference electrode (32) is used to ascertain the potential of the working electrode (22) by way of comparison. The electrochemical cell (100) includes an electrolyte (60).

CARBON ELECTRODES

This application claims priority from AU2012904330 which is incorporated herein in its entirety by reference.

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Technical Field

Disclosed is a process for treating carbon. The process renders the carbon suitable for use as an electrode by modifying the carbon surface. In some embodiments the modification of the surface results in improved functional properties, such as increased reactivity, greater surface area, and improved electrode performance. Also disclosed is a carbon electrode produced by this process.

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When used as an electrode, the treated carbon can be employed in the electrolysis e.g. of water, and thereby replace platinum electrodes, and may also find application in a catalytic converter, again replacing platinum. However, it should be understood that the treated carbon is not limited to such applications.

Background Art

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In the electrolysis of water, hydrogen is produced at the cathode (electrode) of an electrolytic cell and oxygen is produced at the anode (electrode) of the electrolytic cell. Excess power, in the form of an overpotential, is required to be supplied to the electrodes of the cell to overcome various activation barriers, otherwise the electrolysis proceeds slowly. In cells for the electrolysis of water, the anode can be made from a suitable inert metal such as platinum. Such inert metal materials are expensive. In addition, with existing cells and electrolysis processes, competing side reactions can dominate, especially where salts are present in the water.

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Any references herein to the background prior art do not constitute an admission that such art forms a part of the common and/or general knowledge of a person of ordinary skill in the art. The above description is also not intended to limit the application of the process disclosed herein.

Summary of the Disclosure

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Herein described is a method of electrolysing water. The method comprising the steps of preparing a carbon electrode by treating a carbon material with one or more ionic liquids so as to functionalise the surface of the carbon with ions from the ionic liquid. At least one of the one or more ionic liquids has a $\Delta[pka]$ in the range of from about 10 to about 20. The method also includes the step of electrolysing water with the carbon electrode.

The term ionic liquid is herein applied to substances that comprise only of ions and that remain in the liquid state below the boiling point of water and preferably down to room temperature. An ionic liquid has an acid component and a base component.

The acid and base components of the ionic liquid each have a pKa. The pKa of the base component is 14-pKb. The difference between the pKa's of the acid and base components can be represented by the formula:

$$|[pK_{a_{base}}] - [pK_{a_{acid}}]| = \Delta[pK_a]$$

Where pKa(base) is the acidity constant of the base; and pKa(acid) is the acidity constant of the acid.

The $\Delta[pK_a]$ is a measure of the shift in equilibrium of an ionic liquid towards the ionic state. The $\Delta[pK_a]$ of the ionic liquid can be about or greater than 10. A $\Delta[pK_a]$ of about or greater than 10 can result in an ionic liquid that is highly ionised. By highly ionised, it is meant that there is about 80, 85, 90, 95 or 99 % of the species in solution are ionised. If the $\Delta[pK_a]$ is less than about 10 the ionic liquid can be unstable. Furthermore, at a $\Delta[pK_a]$ of less than about 10, neutral species can exist in the ionic liquid which can adversely affect the properties of the ionic liquid, such as the electrochemical properties. In some embodiment, the $\Delta[pK_a]$ is about or greater than 12, 15 or 17.

The ΔpK_a of the ionic liquid can be about or less than 20. A $\Delta[pK_a]$ of greater than about 20 is undesirable. A $\Delta[pK_a]$ of greater than 20 can result in a "drive" for proton transfer between the acid and the base component that is so large that substantially no protons are free to participate in other reactions. In some embodiments, the $\Delta[pK_a]$ is about or less than 19, 17 or 15.

In one embodiment, the $\Delta[pK_a]$ is from about 10 to about 15. In another embodiment, the $\Delta[pK_a]$ is from about 15 to about 20.

Selecting the ionic liquid can include selecting a single ionic liquid that has a $\Delta[pK_a]$ within the range of from about 10 to about 20. Alternatively, a mixture of two or more ionic liquids can be selected provided at least one of the ionic liquids has a ΔpK_a of from about 10 to about 20. In some embodiments each ionic liquid has a $\Delta[pK_a]$ of from about 10 to about 20. The ionic liquid is provided in a solution. The amount of ionic liquid in the solution can be 60, 70, 80, 90 or 95 vol%. The amount of solvent in the solution of ionic liquid can be 10, 20, 30 or 40 vol%. This can result in a solution having, 0.5, 1, 1.5 M of ionic liquid.

The ionic liquid(s) having a $\Delta[pK_a]$ in the range of from about 10 to about 20 can be provided as an aqueous solution. An aqueous solution is advantageous when the resultant

carbon electrode is for the electrolysis of water. This is because the medium in which the ionic liquid is dispersed (i.e. water) is the same as the medium in which the carbon electrode will operate. In some embodiments the one or more ionic liquids are provided in an organic solution. The organic solution and ionic liquid(s) should be miscible. The organic solution
5 can be selected from the group comprising: MeCN, ethanol or methanol.

The $\Delta[pK_a]$ range should be met in the solution in which the carbon material is treated. If the ionic liquid is in an aqueous solution, the $\Delta[pK_a]$ should be within the required range (of from about 10 to about 20) when in that aqueous solution. The pK_a of the ionic components are typically reported in aqueous solution. The pK_a can be measured or
10 determined using literature sources. The $\Delta[pK_a]$ of the ionic liquid can be found in literature or determined experimentally. If the ionic liquid is in organic solution, the $\Delta[pK_a]$ should be within the required range when in that organic solution. The temperature and pressure of any solution can be modified during treatment of the carbon material to achieve a $\Delta[pK_a]$ within the required range.

Also disclosed herein is a method of preparing a carbon electrode for use in the electrolysis of water. The method comprising the step of treating a carbon material in a first cell with one or more ionic liquids so as to functionalise the surface of the carbon material with ions from at least one of the one or more ionic liquids. At least one of the one or more ionic liquids has a $\Delta[pK_a]$ in the range of from about 10 to about 20.
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In one embodiment, the method further comprises the step of electrolysing water using the carbon electrode in a second cell. The second cell is different from the first cell.
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The carbon electrode can be prepared in a first cell in which the surface functionalization occurs. The first cell can be any container suitable for holding and containing the carbon material during functionalization. The first cell may contain one or
25 more electrodes, or there may be no electrodes (this is described in more detail below). The carbon electrode can then be used in a second cell which differs from the first cell. By different it is meant that at least the electrolyte of the cell is replaced. For the electrolytic treatment of water, the ionic liquid electrolyte can be removed and replaced with water. The electrolysis cell can further comprise one or more cathode assemblies. The second cell can
30 be any container suitable for holding a solution to be electrolysed. The electrolysis cell can further comprise one or more cathode assemblies.

Also described is a method of electrolysing water comprising the steps of preparing a carbon electrode by treating a carbon material with one or more ionic liquids so as to functionalise the surface of the carbon with ions from the ionic liquid. At least one of the one
35 or more ionic liquids comprises one or more anions selected from the group consisting of:

RSO_3^- or RCOO^- , where R is an alkyl or a substituted alkyl group; $(\text{CF}_3\text{SO}_3)^-$; $(\text{R}-\text{CF}_2\text{CF}_2\text{SO}_3)^-$; $(\text{CF}_3\text{SO}_2)\text{N}^-$; $(\text{CF}_3\text{SO}_2)_3\text{C}^-$; $\text{CHF}_2\text{CF}_2\text{SO}_3^-$; $(\text{CH}_3\text{CH}_2\text{SO}_4)^-$; and/or mixtures thereof. The method also includes the step of electrolysing water with the carbon electrode.

Also described is a process for treating a material with one or more ionic liquids in a first cell so as to functionalise the carbon. At least one of the one or more ionic liquids comprises one or more anions selected from the group consisting of:

RSO_3^- or RCOO^- , where R is an alkyl or a substituted alkyl group; $(\text{CF}_3\text{SO}_3)^-$; $(\text{R}-\text{CF}_2\text{CF}_2\text{SO}_3)^-$; $(\text{CF}_3\text{SO}_2)\text{N}^-$; $(\text{CF}_3\text{SO}_2)_3\text{C}^-$; $\text{CHF}_2\text{CF}_2\text{SO}_3^-$; $(\text{CH}_3\text{CH}_2\text{SO}_4)^-$; and/or mixtures thereof. The method also including the step of using the treated carbon as an electrode in a second cell which is different from the first cell. The description relating to the first and second cells provided above also applies here.

In one embodiment, the ionic liquid comprises one or more anions selected from RSO_3^- or RCOO^- wherein R comprises at least one electronegative bond. In one embodiment, the electronegative bond is a C-F bond. In one embodiment, R is CF_3^- . In one embodiment, the anion is a triflate ion $((\text{CF}_3\text{SO}_3)^-)$.

The cation of the ionic liquid is thought to be less important than the anion because it is not thought to significantly functionalise the surface of the carbon material. The cation is selected to provide an ionic liquid with desirable viscosity and conductivity. In an embodiment, the cation of the ionic liquid may comprise at least one positively charged nitrogen atom. The cation may comprise a nitrogen-containing aromatic ring. The nitrogen-containing aromatic ring may comprise an imidazolium ring. Protons with a net positive charge may be located on any one of the two nitrogen atoms in the aromatic ring.

In an embodiment, the cation may have the general structural formula:



wherein R^1 and R^2 are independently selected from hydrogen and a hydrocarbonyl group, and wherein the hydrocarbonyl group is an optionally substituted alkyl group, or an optionally substituted cycloalkyl group, or an optionally substituted heteroaryl group.

In one embodiment, the cation that provides the desired viscosity and conductivity is 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIM), 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMIM) or 1-butyl-3-methylpyrrolidinium.

The ionic liquid can be selected from the group comprising 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM][triflate]), 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIM][triflate]) and/or 1-butyl-3-methylpyrrolidinium triflate. These ionic liquids have a $\Delta[\text{pK}_a]$ within the required range.

The ionic liquid having anions selected from the group RSO_3^- or RCOO^- , where R is an alkyl or a substituted alkyl group; $(\text{CF}_3\text{SO}_3)^-$; $(\text{R}-\text{CF}_2\text{CF}_2\text{SO}_3)^-$; $(\text{CF}_3\text{SO}_2)\text{N}^-$; $(\text{CF}_3\text{SO}_2)_3\text{C}^-$; $\text{CHF}_2\text{CF}_2\text{SO}_3^-$; $(\text{CH}_3\text{CH}_2\text{SO}_4)^-$; and/or mixtures thereof can be provided as an aqueous solution. In some embodiments the one or more ionic liquids are provided in an organic solution. The organic solution and ionic liquid(s) should be miscible. The organic solution can be selected from the group comprising: MeCN, ethanol or methanol.

The carbon material is oxidised prior to being functionalised with ions from the ionic liquid. The carbon material treated by the process can be provided directly to the one or more ionic liquids as pre-oxidised carbon. In one embodiment, the method further includes the step of oxidising the carbon material prior to treatment with the ionic liquid. Alternatively, the carbon can be oxidised in situ during formation of the carbon electrode.

The carbon material to be treated may comprise one or more of oxidised or unoxidised forms of: carbon black, a carbon nanofilament, a 3D carbon sieve, activated carbon, graphite, graphene, a carbide-derived carbon material, carbon paper, carbon nanotube, or Buckyballs.

In an embodiment, the carbon material is treated by electrolysis of the carbon material in an electrochemical cell. In this cell, the carbon forms at least part of an electroconductive electrode. By at least a part it is meant that the carbon material can form the whole electrode or a surface part of the electrode. The carbon material may be particulate and be dispersed within the cell. In this cell, the one or more ionic liquids form the electrolyte contacting the electroconductive carbon material in the electrochemical cell. In this embodiment, during the electrochemical treatment the carbon is oxidised and functionalised with the anions of the ionic liquid in the same process.

In this embodiment, the electrochemical cell may further comprise one or more electroconductive counter electrodes. The (or each) electroconductive counter electrode may form part of a counter electrode assembly. When this counter electrode assembly is referred to a standard reference electrode, the voltage drop across the one or more counter electrodes may be less than a voltage drop across the electroconductive electrode. This can enable the carbon material to be functionalised.

The electrochemical treatment of the carbon can include a controlled potential electrolysis of the ionic liquid electrolyte through the application of a direct current. If the current strength is too high, the risk of exfoliating the carbon material is increased and results in vigorous gas evolution. Furthermore, if the current is too high, the carbon material can become an insulator and this can lead to dissolution of the carbon material into solution. Conversely, with low current strength the surface functionalization can take too long. In the process of treating the carbon material, the current density in the range of from about 3, 5, 8

or 10 mA/cm² to about 10, 15, or 25 mA/cm² across the working electrode (the carbon material) and the counter electrode. In one embodiment, the current strength is from about 8 to about 15 mA/cm².

The voltage drop across the working electrode with reference to the reference electrode can be less than the voltage drop across the counter electrode (i.e. with reference to the reference electrode). As a result, the working electrode can act as an anode (A) and the counter electrode can act as a cathode (C). Voltages in the range of from about 1, 1.5, 2 or 2.5 V to about 2, 2.5, 3 or 3.5 V (vs. the reference electrode) can be applied.

In another embodiment, oxidised carbon can be contacted with one or more ionic liquids and the mixture can be mechanically agitated in order to encourage surface functionalization. The mechanical agitation is undertaken to cause the carbon surface to be functionalised with ions from the ionic liquid. The mechanical agitation can be selected from one or more of exfoliation, grinding and high shear mixing.

Optionally, there can be sonication or ultrasonication during the agitation to facilitate the reaction. In one embodiment, an ionic liquid gel can be formed by ultrasonication and grinding of oxidised carbon in the presence of one or more ionic liquids.

Once the carbon has been treated by the ionic liquid, the carbon electrode can be collected for use. The carbon electrode can be removed from the ionic liquid and used without further treatment. The removal can be by any means that separates the carbon electrode from the ionic liquid. In some embodiments, in particular when the carbon is particulate, the carbon electrode can be removed from the ionic liquid by filtration. The filtrate can then be formed into a shaped carbon electrode. The step of forming the treated particulate carbon into a shaped electrode may include pressing the carbon into the desired shape.

It has been observed that an ionic liquid can chemically modify the carbon surface. In an embodiment, following treatment, the functionalised carbon material can comprise one or more functional groups selected from ionised or unionised forms of one or more of: -COOH, -CHO, -CO-, -OSO₃H, -OH, SO₃⁻, -C-F, -NC₂, NC₃⁺.

It has further been observed that the resultant modified surface can have improved functional properties including increased reactivity, greater surface area, and improved performance when used as an electrode.

In an embodiment, the treating of the carbon can result in a lowering of over-potential of the resultant carbon electrode with reference to an initial onset potential of the electrode. This can render the treated carbon suitable for use in the oxidation of water.

The functionalised treated carbon electrode can comprise one or more derivatives of the one or more anions of the ionic liquid. The ions may have fragmented or changed

before functionalising the surface of the carbon material, but they are still from the ionic liquid.

During treatment, the anions can assemble at the interface between the carbon surface and the ionic liquid. At least some of the anions may be physisorbed at the surface of the carbon by electrostatic attraction. In some embodiments, the anions may be otherwise attached to the carbon surface by e.g. Van der Waal forces, by covalent and/or by dative bonds.

The treatment of the carbon surface can occur over time. The treatment can occur for a period of time sufficient to result in about 50, 60, 70, 80, 90 or 95 % of the surface area being functionalised. However, the treatment need only be for a period of time sufficient of the resultant treated carbon to be functional as a carbon electrode for the electrolysis.

When the carbon is treated electrochemically, the treatment time may be at least about 20, 30, 45, 60, 75, 90, 120 or 180 minutes. When the carbon is treated mechanically, the treatment time may be about 10, 20, 30 or 45 minutes.

When the carbon material has been functionalised the change in the surface properties can be detected by water contact angle changes. In some embodiments, the water contact angle is reduced to zero, or close to zero as the surface becomes hydrophilic. The functionalisation can also be detected by XPS data.

In an embodiment, treating the carbon may result in an increase in basal spacing of the carbon material. For example, functionalisation of the carbon material may result in an increase in basal spacing of the carbon material.

In an embodiment, treating the carbon may result in an increase in surface area of the carbon material contacting the electrolyte. The increase in surface area may be 10, 20, 30 or 40 % increase in surface area as compared to the carbon before treatment by the process.

Also disclosed herein is a process of electrolysing water. The process comprises contacting a first electrode and a second electrode with water. In the process the first electrode comprises a functionalised carbon material including one or more functional groups selected from the following: -COOH, -CHO, -CO-, -OSO₃H, -OH, SO₃⁻, -C-F, -NC₂, NC₃⁺.

Also disclosed herein is an electrode produced by the process as disclosed herein. The electrode can be for the electrolytic treatment of water. The water is split to produce hydrogen and oxygen. The water can contain a solute. The water can contain 25, 35, 50, 60, 75 or 80 vol% of a solute. The solute can be a salt. The carbon electrode can be used to electrolyse a brine solution (sodium chloride dissolved in water) to generate chlorine. The chlorine can be generated as a gas.

In an embodiment the process of electrolysing water may be conducted in an electrolysis cell. Use of the carbon electrode prepared by the above described process can result in an onset potential for the working carbon electrode to be observed at a much lower value compared to known processes. The lower value can be 1, 1.05 or 1.10 V vs NHE.

5 The electrolysis of a solution can be undertaken for any period of time sufficient to achieve the desired reaction. In one embodiment, the electrolysis is undertaken for 5, 15, 25, 45, 60 or 75 minutes.

The process can further include the step of adding a catalytic additive to the surface of the prepared carbon electrode. The catalytic additive can further improve the ability of the carbon electrode to electrolyse water. The catalytic additive can comprise a noble metal and/or a platinum group metal. The catalytic additive can be selected from the group comprising gold, platinum, palladium, rhodium, ruthenium. The catalytic additive can comprise a chalcogen ion together with an electropositive element (a chalcogenide). In one embodiment, the catalytic additive is cadmium telluride, indium sulfide, zinc telluride, and/or sodium selenide. In one embodiment, the catalytic additive is a dichalcogenide which contains two atoms of chalcogen per molecule or unit cell; or is any compound containing two different chalcogens.

The catalytic additive can be added to the surface of the carbon electrode by a technique such as printing, sputtering and/or contact adhesion. In some embodiment, the catalytic additive is added by chemical reduction of metal salt (as appropriate); by microwave reduction; wet-impregnation; or in-situ chemical methods. The means by which the surface is decorated with the co-catalyst is not limited.

Brief Description of the Drawings

25 Notwithstanding any other forms which may fall within the scope of the process and electrode as set forth in the Summary, specific embodiments will now be described, by way of example only, with reference to the accompanying drawings in which:

Figure 1 shows a first embodiment of a process for treating carbon in an electrochemical cell.

30 Figure 2 shows a second embodiment of a process of electrolytic oxidation of water.

Figure 3A shows a water contact angle for carbon in the form of graphite of Example 1 before electrochemical treatment of Example 1. Figure 3B shows a water contact angle for carbon in the form of graphite of Example 1 after electrochemical treatment.

35 Figure 4(a) is a spectrum of carbon from Example 1 before the electrochemical treatment of Example 1 obtained by X-Ray Photoelectron Spectroscopy (XPS).

Figure 4(b) is a comparative spectrum to Figure 4(a), with (i) indicating a spectrum obtained by XPS before the electrochemical treatment of Example 1, and with (ii) indicating a spectrum obtained by XPS after the electrochemical treatment of Example 1.

Figures 4(c) to 4(f) show the C_{1s} , F_{1s} , S_{2p3} and N_{1s} spectra obtained by XPS for the sample of example after undergoing electrochemical treatment.

Figure 5 is a diffractogram obtained by X-Ray diffraction (XRD) of the graphite of Example 1 after the electrochemical treatment of Example 1.

Figure 6A shows the variance of current (I) with varying applied voltage (V Ag/AgCl) during electrolysis of water using the carbon electrode in example 1 and is compared with a treated Platinum electrode.

Figure 6B shows Tafel plots obtained for the electrode of comparative example 2 and the graphite electrode prepared in Example 1 after electrochemical treatment.

Figure 7 shows Cyclic Voltammograms (CVs) of the graphite electrode of Comparative Example 2 and of the graphite electrode of Example 1 after electrochemical treatment.

Figure 8 shows oxygen evolution over a time scale on a graphite electrode of Example 1 during water oxidation.

Figure 9 shows the time vs. current of the treatment of carbon electrode B at a constant potential of 1.9V vs. Ag/AgCl.

Figure 10 shows a Cyclic Voltammogram (CV) of carbon electrode B.

Figure 11 shows oxygen evolution over a time scale on carbon electrode B during water oxidation.

Figure 12A shows the time vs. current of the treatment of carbon electrode C at a constant potential of 1.9V vs. Ag/AgCl.

Figure 12B shows the time vs. current of the treatment of carbon electrode D at a constant potential of 1.9V vs. Ag/AgCl.

Figure 13A shows a Cyclic Voltammogram (CV) of carbon electrode C.

Figure 13B shows a Cyclic Voltammogram (CV) of carbon electrode D.

Figure 14A shows an attempt to measure oxygen evolution over a time scale on carbon electrode C during water oxidation.

Figure 14B shows an attempt to measure oxygen evolution over a time scale on carbon electrode D during water oxidation.

Figure 15 shows untreated graphite (black line) and treated graphite (red line) cycled through the range of voltages shown on the horizontal axis.

Figure 16 shows that the first cycle (black line) is overlaid with the 1000th cycle (red line).

Figure 17 shows that treating in a pure(er) ionic liquid produces a more catalytically active electrode (red line), compared to an electrode treated in diluted ionic liquid (blue line).

Detailed Description of Specific Embodiments

Referring to Figure 1, a non-limiting embodiment of a process 1000 for treating a carbon material is schematically depicted. Carbon in the form of a carbon allotrope, graphite 10, is electrochemically-treated in an electrochemical cell 100. The electrochemical cell 100 includes two cell compartments, a first electrochemical cell compartment 20 and a second electrochemical cell compartment 40. The first compartment 20 and the second compartment 40 are separated by glass frit 70. The electrochemical cell includes a working electrode assembly 25 that is contained in the first compartment 20. The working electrode assembly 25 includes a working electrode 22. Graphite 10 forms at least a part of the working electrode 22. A counter electrode assembly 45 is contained in the second compartment 40. A platinum wire 46 forms a counter electrode 42 in the counter electrode assembly 45. A reference electrode assembly 30 with a reference electrode 32 is used to ascertain the potential of the working electrode 22 by way of comparison.

The electrochemical cell 100 includes an electrolyte 60. In this embodiment, the electrolyte 60 comprises an aqueous solution containing triflate anions ($\text{CF}_3\text{-SO}_3^-$) ($\text{pKa} = -7$) and cations with a nitrogen containing imidiazolium ring having the general structural formula:



wherein R^1 and R^2 are independently selected from hydrogen and a hydrocarbyl group, and wherein the hydrocarbyl group is an optionally substituted alkyl group, or an optionally substituted cycloalkyl group, or an optionally substituted heteroaryl group. When R^1 is butyl and R^2 is methyl the pKa of the imidiazolium ring is 7.5. The $\Delta[\text{pKa}]$ of the anion-cation pair is therefore 14.5.

The process of electrochemically treating graphite 10 includes a controlled potential electrolysis of the electrolyte 60 through the application of a direct current with a current density in the range of $5\text{mA}/\text{cm}^2$ to $25\text{mA}/\text{cm}^2$ across the working electrode 22 and the counter electrode 42. The voltage drop across the working electrode 22 with reference to the reference electrode 32 is less than the voltage drop across the counter electrode 42 (i.e. with reference to the reference electrode). As a result, in this embodiment, the working electrode 22 acts as an anode (A) and the counter electrode 42 acts as a cathode (C). Voltages in the range of 1V to 3V (vs. the reference electrode 32) are applied to the

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electrochemical cell 100 across the working electrode 22 (with graphite 10) and the counter electrode 42 for a duration in the range of 20 minutes to 2 hours.

Electrochemical treatment of the graphite 10 forming the working electrode 22 in the electrolyte 60 containing triflate anions $(CF_3-SO_3)^-$ surprisingly introduces functional groups onto a surface 12 of the graphite 10 on the working electrode 22. The functional groups include: $-COOH$, $-CHO$, $-CO-$, $-OSO_3H$, $-OH$, SO_3^- , $-C-F$, $-NC_2$, NC_3^+ . Without wishing to be bound by theory, it is understood that at least some of the aforementioned functional groups are introduced as a result of oxidation of the graphite 10 on the working electrode 22. The electrochemical treatment of the graphite 10 can also surprisingly results in catalytic sites being formed on the surface of the graphite 10. Electrochemical treatment of the graphite 10 can also surprisingly results in an increase in basal spacing of the graphite 10.

It is also noted that a negatively charged anion species, such as the triflate group $(CF_3-SO_3)^-$, has as a negative charge spread over three oxygen atoms and a sulphur atom. Triflating agent comprising anions such as $(CF_2SO_3^-)_2$; $(CF_2CF_2SO_3^-)_2$; $(CF_3SO_2^-)_n$; $(CF_3SO_2)_3C$ also have a negative charge spread over and the oxygen and sulphur atoms, and also include C-F and SO_3 linkages within their structure. Without wishing to be bound by theory, it is understood that functional groups of C-F and SO_3 may be functionalised on the graphite 10 of the working electrode 22 as a result of oxidation of the graphite 10, thereby electrochemically treating the graphite 10.

Without wishing to be bound by theory, it is understood that the process 1000 results in the attachment of functional groups on the graphite 210 including: $-COOH$, $-CHO$, $-CO-$, $-OSO_3H$, $-OH$, SO_3^- , $-C-F$, $-NC_2$, NC_3^+ . This is thought to result in the lowering of the onset potential of the working electrode.

The carbon electrode prepared according to the above process can optionally be modified with one or more catalytic additives. The catalytic additive can be selected from a noble metal and/or a platinum group metal.

Referring now to Figure 2, a non-limiting embodiment of a process 2000 for carrying out electrolytic oxidation of water will be described. A carbon electrode in the form of a functionalised carbon allotrope – graphite 210 is placed in an electrochemical cell 2100 for the electrolytic splitting of water (H_2O). The water electrolysis process in electrochemical cell 200 consists of two half reactions, a hydrogen formation reaction and a water oxidation reaction. It is to be appreciated by a skilled person in the art that electrolytic oxidation of water may result in oxygen evolution and other products such as but not limited to Hydrogen Peroxide.

In this embodiment the electrochemical cell 200 comprises two compartments, a first electrochemical cell compartment 220 and a second electrochemical cell compartment

240. The first compartment 220 and the second compartment 240 are separated by glass frit 260. The electrochemical cell includes a working electrode assembly 225 that is contained in the first compartment 220. The working electrode assembly 225 includes a working electrode 222. Treated graphite 210 forms at least a part of the working electrode 225 in the preferred embodiment. A counter electrode assembly 245 is contained in the second compartment 240. A platinum wire 246 forms a counter electrode 242 in the counter electrode assembly 245. A reference electrode assembly 230 with a reference electrode 232 is used to ascertain the potential of the working electrode 222 by way of comparison.

The process of electrolytic water splitting includes a controlled potential electrolysis of the aqueous electrolyte 260 carried out by application of a direct current with a current density in the range of $5\text{mA}/\text{cm}^2$ to $25\text{mA}/\text{cm}^2$ across the working electrode 222 and the counter electrode 242. The voltage drop across the working electrode 222 is less than the voltage drop across the counter electrode 242 (i.e. with reference to the reference electrode 232). As a result, the working electrode 222 acts as an anode (A) and the counter electrode 242 acts as a cathode (C). Voltages in the range of 1V to 3V (vs. the reference electrode 242) were applied to the electrochemical cell 200 across the working electrode 222 (with graphite 210) and the counter electrode 242 for a duration in the range of 20 minutes to 2 hours.

An initial water oxidation was observed at the working electrode 222 with a water oxidation response having an onset potential of around 1.5 V. An applied potential larger than 1.75 V is required to achieve a current density larger than $1\text{mA}/\text{cm}^2$, which corresponds to the overpotential of more than 900 mV. (Water oxidation potential(E) is pH dependent, $E = 1.23 - 0.059\text{pH}$. At pH 7, the thermodynamic oxidation of water is 0.817 V vs. NHE).

It is noted that prior art processes for electrolytic oxidation of water require applied potentials to be greater than that of theoretical reversible potential of 1.23 V to facilitate water oxidation. Typically this excess potential accounts for various forms of overpotential by which the extra energy is eventually lost, for example as heat etc.

Surprisingly, it is observed that, after an operating period in the range of 5 minutes to 60 minutes of the process 2000, the onset potential for the working electrode is observed at a much lower value of approximately 1.05 V vs. NHE, with gas bubble formation being visible on the surface of the working electrode 222. Furthermore, a current density of $4\text{mA}/\text{cm}^2$ is obtained when the potential reaches 1.2 V vs. NHE with a much lower calculated overpotential of 380 mV only.

It should be mentioned that the process can also be carried out at controlled current mode, which may be preferred for scaled-up applications. The optimal conditions for constant current pre-treatment are currently being investigated.

5 Examples

A process of treating a carbon material will hereinafter be described in detail, by way of non-limiting examples thereof.

In the following Examples, electrochemical treatment processes were carried out with a CHI 760 Electrochemical Workstation (Texas, USA). Electrochemical treatment was
10 conducted at in a two-compartment electrochemical cell separated by a glass frit (Figures 1 and 2). Graphite rod or graphite paper was used as the working electrode and a platinum wire was applied as the counter electrode. An Ag/AgCl reference electrode assembly (BASi, IN, USA) was used as the reference electrode.

In the following examples graphite, in the form of graphite rods, was purchased
15 from Goodfellow (Huntingdon, England) with a diameter of 3mm and purity of 99.997%. Carbon paper was received from Fuel Cell Store (Colorado, USA), which was made of graphite fibers.

Water used in the following examples was purified by a MilliQ water purifying system, which has a resistance of 18.2 Ω M. Phosphate buffer solution (pH = 7) was
20 prepared by dissolving potassium hydrogen phosphate (KH_2PO_4) and potassium phosphate monobasic (KH_2PO_4) in water, and the pH was adjusted by 1 M KOH or 1 M H_2SO_4 .

In the following Examples, Scanning Electron Microscopy (SEM) measurements were carried out with a FEI Nova NanoSEM 230 field emission SEM (FESEM) at 10 kV. X-ray photoemission spectroscopy (XPS) elemental analysis was conducted on a Kratos
25 AXIS imaging XPS microprobe and Auger system used to characterise the surface functionality of graphite. All spectra were calibrated with the C 1s which is of sp^2 hybridised carbon peaked at 284.8 eV. X-Ray Diffraction (XRD) was carried out on a PANalytical X'Pert instrument.

Oxygen produced in the following examples was qualitatively detected by a
30 fluorescent-based oxygen sensor (Oceanic Optics USA).

Example 1

In a first example, carbon in the form of graphite was electrochemically-treated in an electrochemical cell with the CHI 760 Electrochemical Workstation (Texas, USA).
35 Graphite in the form of graphite rod and/or graphite paper was used as a working electrode in the electrochemical cell. A platinum wire was applied as the counter electrode and the

Ag/AgCl reference electrode assembly was used as a reference electrode for the electrochemical cell. The electrolyte for the electrochemical cell was an aqueous solution of 1 M 1-butyl-3-methylimidazolium trifluoromethanesulfonate [BMIM][triflate]. In particular, a controlled potential electrolysis of the aqueous electrolyte was carried out. The graphite used as (or part of) a working electrode was electrochemically-treated by way of applying a potential of approximately 1.9 V vs. Ag/AgCl across the working electrode (and the counter electrode) for a time duration of approximately 1 hour. A potential at 1.9 V vs. Ag/AgCl was chosen to treat the graphite in the 1M [BMIM][triflate]. Advantageously, at this potential, the exfoliation of graphite as well as dissolution of carbon compounds was observed to be negligible, whilst a considerate rate of treatment was preserved.

It was noted that potential was an important parameter for controlled electrochemical treatment of graphite. High potential generated high current density (j), which shortened the treatment time. However, high current strength risked exfoliating graphite with vigorous gas evolution. Furthermore, it was noted from the literature that, when j was higher than a certain amount (>25 mA), violent oxidation of graphite itself would take place (completely oxidised graphite then becomes an insulator), leading to the dissolution of carbon components into an electrolyte solution. Conversely, with low potential, resulting in a small value of j , it would take excessive time to complete the electrochemical treatment process. The j in the present Example increased steadily after the commencement of the reaction, and reached a maximum of 9 mA cm^{-2} after 1800 sec. The reaction time was therefore controlled to 1 hour, in order to introduce sufficient catalytic sites onto the surface of the graphite. The electrochemically-treated graphite electrode was thereafter recovered and dried at room temperature.

The water contact angle for the electrochemically-treated graphite was analysed before electrochemical treatment of the graphite in Figure 3A and after electrochemical treatment in Figure 3B. The surface of the electrochemically-treated graphite in Figure 3B was observed to be super-hydrophilic and no water contact angle (a contact angle of zero degrees) was observed.

Without being bound by theory, it was understood that during the course of treatment of graphite in [BMIM][triflate], the graphite was mildly oxidised and was functionalised, being decorated with oxygen-containing functional groups, which increased the hydrophilicity of the surface of graphite dramatically. It was understood that these hydrophilic oxygen-containing functional groups served as active catalytic sites, and facilitated the adsorption of water molecules, as well as facilitating water oxidation and subsequently reducing the energy barrier needed to overcome the oxidising of water.

Oxidation of the graphite, due to the electrochemical treatment in 1 M [BMIM][triflate], was also indicated by the spectra obtained by X-ray photoelectron spectroscopy (XPS) of the electrochemically-treated graphite before and after the electrochemical treatment, respectively. Figure 4(a) indicates a relatively small O_{1s} photoemission peak on the surface of the graphite before the electrochemical treatment. Such a peak was ascribed to oxygen physically adsorbed onto graphite from air. After the electrochemical treatment of the graphite with [BMIM][triflate] in the electrochemical cell, the intensity of O_{1s} peak appeared to increase dramatically due to the introduction of a large amount of oxygen-containing functional groups. Furthermore, a C_{1s} peak of the electrochemically-treated graphite was noted to be fitted into four Gaussian-Lorentzian shape peaks, besides two peaks belonging to sp² hybridised graphite, which centered at 284.91 eV and 285.77 eV, respectively. Two additional peaks attributed to C-O (297.08 eV) and O=C-OH (288.8 eV) were also observed as a result of the electrochemical oxidation of the graphite in [BMIM][triflate]. Besides oxygen-containing groups, F_{1s}, S_{2p3} and N_{1s} peaks were also observed in the XPS spectra after treatment, suggesting functionalisation of the electrochemically-treated graphite by functional groups such as COOH, -CHO, -CO-, -OSO₃H, -OH, SO₃⁻, -C-F, -NC₂, NC₃⁺. A layer of [BMIM][triflate] also appeared to form on the surface of the electrode of Example 1. In Figure 4(e) and Figure 4(f), the presence of F-C and -SO₃⁻ from the [triflate] group in [BMIM][triflate] were observed at 688.52 eV and 169.52 eV, respectively. The N_{1s} spectra was able to be fitted into two peaks (Figure 7(g)), which belonged to -NC₂ (401.54 eV) and -NC₃⁺ (400.1 eV) groups of the [BMIM], respectively. The XPS suggested the presence of oxygen-containing functional groups, as well as [BMIM][triflate] layers on the surface of graphite after electrochemical treatment of the graphite, both of which were surmised to have a contributory effect on the overall catalytic activity of the graphite.

X-ray diffraction (XRD) spectroscopy was used to detect the change of crystalline structures of graphite before and after electrochemical treatment. The sharp (002) peak of pristine graphite was observed to peak at 26.35 (Figure 5) suggesting an interlayer distance of 0.337 nm. After treatment, this peak decreased slightly to 25.98, which corresponded to an increase of interlayer distance of 0.345 nm. The slight increased basal spacing of graphite after treatment was surmised to relate to the opening of the graphitic edge, with the introduction of oxygen-containing groups during electrochemical treatment, which was also surmised to contribute to the increase in effective surface area.

In the following Example, the electrochemically-treated graphite electrode was referred to as "*Example 1*" for the sake of brevity (unless stated otherwise).

Comparative Example 2

A graphite electrode without any electrochemical pre-treatment was used in Comparative Example 2.

5 Differences in Electrochemical Behaviour between Electrode of Example 1 and Electrode of Comparative Example 2

Electrochemical behaviour differences between the electrode of Example 1 and the electrode of Comparative Example 2 were analysed by way of carrying out electrolytic oxidation of water in the electrochemical cell with the CHI 760 Electrochemical Workstation
10 (Texas, USA). Both the cell compartments were filled with 0.1 M phosphate buffer, which was degassed with high purity N₂ for more than 1 hour before water oxidation reactions were carried out.

Figure 6(a) illustrates a comparison of the I-V characteristics of the carbon electrode of example 1 and pre-treated Platinum electrode. To prepare the pre-treated
15 Platinum electrode, a standard Platinum electrode (>99%) was treated using an electrochemical treatment process that is identical to the treatment process used for preparing the carbon electrode in example 1.

A working electrode made from graphite of the process of Example 1 showed an overpotential for water oxidation that was significantly less than the overpotential observed
20 for a platinum electrode. More specifically, Figure 6(a) shows that significant capacitance current was observed with the electrode of Example 1 prior to the onset potential of water oxidation. Without being bound by theory, it was understood that capacitance current observed for the graphite electrode prepared by the process of Example 1 was due to an increased surface area of the graphite. The increased surface area was a result of the
25 electrochemical treatment of the graphite in Example 1. The onset potential for water oxidation for the graphite electrode of Example 1 was observed to be at approximately 1.05 V vs. NHE, with gas bubble formation at its surface. The graphite electrode prepared by the process of Example 1 had a current density of 4 mA/cm² at a potential of 1.2 V vs. NHE with a calculated overpotential of only 380 mV. Oxygen evolution at the electrode of Example 1
30 was confirmed by detecting a steady increase of oxygen concentration by way of the fluorescent oxygen sensor.

Figure 6(b) shows Tafel plots obtained for the electrode of Comparative Example 2 and the graphite electrode prepared by electrochemical treatment in Example 1. The linearity of the curves of Example 1 and Comparative Example 2 indicated that
35 electrochemical treatment of graphite by the electrochemical process of Example 1 did not reduce the conductivity of the graphite of Example 1. In addition, the Tafel plots did not

indicate any difference in conductivity between the electrochemically-treated graphite of Example 1 and Comparative Example 2.

Further, a remarkable improvement of water oxidation catalytic activity profile indicated that the electrodes of Example 1 alone can be used as an efficient electrode for water oxidation, even without decoration by metal-based catalysts.

In some embodiments, however, metal based catalysts can be added to the electrode.

Figure 7 displays cyclic voltammograms (CVs) of the graphite electrode of Comparative Example 2 and the graphite electrochemically-treated by the process of Example 1. The CV voltammograms were obtained with 0.1 M phosphate buffer (pH 7) in both cell compartments of the electrochemical cell and in a potential range of -0.2 V ~ 0.8 V vs. Ag/AgCl at a scan rate of 10 mV/s.

Figure 7 indicates that the graphite electrode of Comparative Example 2 exhibited a stabilised charging current at around 2.0×10^{-7} A. In contrast, the stabilised charging current for the graphite electrode electrochemically-treated by the process of Example 1 increased more than 20000 times, and a value of ~ 2.3 mA was recorded. Without being bound by theory, it was understood that such an increase in the stabilised charging current for the graphite treated by the process of Example 1 was due to the significantly increased surface area of the graphite electrode of Example 1.

Furthermore, capacitance CV scans of the graphite electrodes of Example 1 in 0.1 M PBS were also recorded at different scan rates. The double layer capacitances per unit area (C_{dl}) for the graphite electrode of Example 1 were obtained by plotting the capacitance currents (i_c) at a selected potential range, where no Faradic process was evident, versus scan rates (v). Under ideal conditions, the relationship $i_c = C_{dl} v$ exists. In this Example, a C_{dl} of 0.033 F/cm^2 was obtained from the graphite of Example 1. The significantly increased surface area and high C_{dl} indicated that the graphite electrodes of Example 1 were potentially useful for a number of applications, including as supercapacitors.

Water oxidation performance of the graphite electrode of Example 1 for water electrolysis was evaluated in the electrochemical cell with the CHI 760 Electrochemical Workstation (Texas, USA). 0.1 M phosphate buffer solution (pH = 7) was used as an electrolyte in both compartments of the electrochemical cell. An oxygen sensor was placed in the headspace of the cell to detect the production of O_2 and, the cell was stirred during the course of water electrolysis using a magnetic stirrer. Before the experiment, the cell was purged with high purity nitrogen for 1 hour to remove dissolved oxygen.

Figure 8 shows the detection of oxygen using the graphite electrode of Example 1 as a working electrode at an applied potential of 1.0 V vs. Ag/AgCl. At this potential,

vigorous gas evolution was observed on the surface of the graphite electrode of Example 1, and the electrolysis current (j) stabilised at nearly 1 mA / cm² after 1000 sec from the commencement of electrolysis. Figure 8 also shows the oxygen concentration profile during the course of electrolysis. Further, Figure 8 shows that after purging with N₂ prior to the commencement of the water electrolysis process, and until time period S (shown in Fig. 8) of 30 minutes, no O₂ was detected for half an hour, indicating the electrochemical cell was gastight. After the commencement of water electrolysis at time period S, by applying a potential of 1.0V vs NHE, the oxygen level increased immediately after the start of electrolysis. When the electrolysis was terminated at time period E (shown in Fig. 8), the oxygen partial pressure stabilised at a partial pressure of approximately around 80 torr, without further increase. Detection of oxygen in a cell compartment containing the graphite electrode of Example 1 indicated that electrolysis of water by applying a potential of 1.0 V was achieved.

In contrast, an electrode of Comparative Example 2 was used as a working electrode at an applied potential of 1.0 V vs. Ag/AgCl. At this potential, current density (j) was very low suggesting no appreciable water electrolysis occurring. No gas evolution was observed on the surface of the graphite electrode of Comparative Example 2. Oxygen concentration monitored by the oxygen sensor for the electrode of example 2 shows no significant change over a period of 10 min. After purging with N₂ prior to the commencement of the water electrolysis process, no O₂ was detected at a potential of 1.0 V vs. Ag/AgCl, and the current density (j) was recorded to be 0.01 mA/cm², suggesting no appreciable water electrolysis occurring at a potential of 1V vs Ag/AgCl with the graphite electrode of Comparative Example 2.

Example 3

In this example, carbon in the form of graphite was electrochemically-treated in an electrochemical cell with the CHI 760 Electrochemical Workstation (Texas, USA). Graphite in the form of a graphite rod and/or graphite paper was used as a working electrode in the electrochemical cell. A platinum wire was applied as the counter electrode and the Ag/AgCl reference electrode assembly was used as a reference electrode for the electrochemical cell.

In two separate experiments, the electrolyte for the electrochemical cell was an aqueous solution of:

A: 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [EMIM][triflate] ($\Delta pK_a = 14.3$)

B: 1-butyl-3-methylpyrrolidinium triflate ($\Delta pK_a = 12.25$)

In each of these examples a controlled potential electrolysis of the aqueous electrolyte was carried out. The graphite used as a working electrode was electrochemically-treated by applying a potential of approximately 1.9 V vs. Ag/AgCl across the working electrode (and the counter electrode) for a time duration of approximately 1 hour. A potential at 1.9 V vs. Ag/AgCl was chosen to treat graphite in a 1M solution. Advantageously, at this potential, the exfoliation of graphite as well as dissolution of carbon compounds was observed to be negligible, whilst a considerate rate of treatment was preserved.

In each experiment the reaction time was controlled to about 1 h, in order to introduce sufficient catalytic sites onto the surface of the graphite. The electrochemically-treated graphite electrode was thereafter recovered and dried under room temperature.

The carbon electrode created from ionic liquid B is referred to as carbon electrode B. Figure 9 shows the time vs. current of the treatment of carbon electrode B at a constant potential of 1.9V vs. Ag/AgCl. The linear nature of the current suggests stable surface modification.

The electrodes created were then used in the electrolysis of water. To test the durability of the treatment process above, Figure 10 displays a cyclic voltammogram (CV) of carbon electrode B in potassium ferrocyanide. The carbon electrode B showed good stability throughout the experiment, suggesting the treatment process is permanent and robust.

Figure 11 shows the evolution of hydrogen using carbon electrode B as a working electrode, swept linearly from -0.6V to 2.0V vs. Ag/AgCl. Above 1.2V, vigorous gas evolution was observed on the surface of the electrode.

Comparative Example 3

Under the same conditions as described in Example 3, the following two ionic liquids were tested (separately). These ionic liquids have a ΔpK_a outside of the range of about 10 to about 20.

C: 1-butyl-3-methylimidazolium iodide ($\Delta pK_a = -1$)

D: 1-butyl-3-methylimidazolium hydrogen sulfate ($\Delta pK_a = 5.58$)

The carbon electrodes created from ionic liquids C and D are referred to as carbon electrodes C and D respectively.

Figure 12A shows a dramatically varying current for electrode C, suggesting unstable treatment and additional, undesirable surface reactions. Figure 12 B shows stable treatment for carbon electrode D. The graph of Figure 12A shows rapid deterioration of carbon electrode C during formation, with visible build-up on the surface of carbon electrode C during treatment.

Figure 13A displays a cyclic voltammogram (CV) of carbon electrode C in potassium ferrocyanide. After three cycles there was catastrophic deterioration of the electrode. Figure 13B displays a cyclic voltammogram (CV) of carbon electrode D in potassium ferrocyanide. The graph is oddly shaped and inefficient.

Figure 14A shows the Linear Sweep Voltammetry (LSV) from -0.2V to 2.0V using carbon electrode C as a working electrode, measured vs. Ag/AgCl. The graph of Figure 14A shows erroneous results indicating that the electrode is not operating properly, with gas evolution at a potential inconsistent with hydrogen production. Figure 14B shows the LSV from -0.6V to 2.0V using carbon electrode C as a working electrode, measured vs. Ag/AgCl. The graph of Figure 14B suggests production of undesirable compounds and inefficient hydrogen production.

Example 4

10g of Carbon Black was dispersed in 100ml of 1M Ionic Liquid using a High-Shear Mixer at 24000rpm for 20mins. If the liquid was too viscous the temperature was increased to 80°C and the shear mixing was repeated. The suspension was subject to centrifugal force at 6000rpm for 4hrs or until the carbon had precipitated.

The ionic liquid solution was decanted leaving behind the treated carbon electrode in particulate form. The coated carbon was pressed into a desired shape through a 10 to 50 micron filter paper.

The decanted ionic liquid was centrifuged and distilled for reuse.

Example 5

10g of Carbon Nanotubes were dispersed in 100ml of 1M BMIM Triflate using a High-Shear Mixer at 24000rpm for 20mins. If the liquid was too viscous the temperature was increased to 80°C and the shear mixing was repeated. The suspension was subject to centrifugal force at 6000rpm for 4hrs or until the carbon nanotube gel phase had precipitated.

The ionic liquid solution was decanted leaving behind the treated carbon electrode in particulate form. The coated carbon was pressed into a desired shape through a 10 to 50 micron filter paper.

The decanted ionic liquid was centrifuged and distilled for reuse.

Example 6

In this example, carbon in the form of graphite was electrochemically treated in accordance with the procedure described in Example 2. Following that procedure, it was

noted that a metal catalyst in the form of Platinum metal particles was able to be deposited on the electrochemically treated graphite electrode by magnetron sputtering of Platinum (Pt). In the case of graphite paper, it was noted that each side of the graphite paper was able to be sputtered with Pt particles. In the sputtering operation, it was noted that the graphite electrode (graphite rod or graphite paper) was able to be placed in a vacuum chamber and the base pressure of the chamber was able to be maintained at approximately 13.3mPa (10^{-4} Torr) or less. It was noted that the Pt source used in this example was able to be in the form of a Platinum foil with 99.95% purity. For carrying out the sputtering of the functionalised graphite electrode, it was noted that a magnetron sputtering machine with a 15.24cm (6") diameter was able to be used to sputter Pt particles at a current rate of 2-3 Amperes/second for a time period of approximately 3 minutes. It was noted that sputtering at such rates was able to result in Pt loaded functionalised graphite electrodes with loading of approximately 0.1mg Pt/cm² on the functionalised graphite electrodes with an approximate thickness in the range of 5nm to 50nm.

Whilst specific embodiments of a process of modifying carbon and an electrode have been described, it should be appreciated that the process and electrode may be embodied in other forms.

Example 7

In Figure 15, a sample of untreated graphite (black line), and treated graphite (red line) were cycled through the range of voltages shown on the horizontal axis. The vertical axis shows the treated graphite conducting 73% more current than the untreated sample. Current is correlated with gas production volume, so this behaviour is highly desirable for electrolysis.

With this desirable behaviour established, the question of durability arises. Treatment degradation can be characterised by continually cycling the electrode over a number of hours, then comparing the first and last cycles. Figure 16 shows that the first cycle (black line) is overlaid with the 1000th cycle (red line). This means that no significant degradation of the carbon electrode occurs under normal electrochemical characterisation conditions. (Small bumps in first cycle is noise).

Both of these results paint a positive picture of the treatment process, which gives graphite favourable characteristics for electrolysis.

Figure 17 shows that treating in a pure(er) ionic liquid produces a more catalytically active electrode (red line), compared to an electrode treated in diluted ionic liquid (blue line). The increased catalytic activity is represented by a greater distance away from the horizontal axis, i.e. bigger current in both positive and negative directions.

The term "alkyl" as used herein, either alone or in a compound word such as "optionally substituted alkyl" or "optionally substituted cycloalkyl", is to be understood to denote straight chain, branched or mono- or poly- cyclic alkyl, preferably C₁₋₃₀ alkyl or cycloalkyl. Examples of straight chain and branched alkyl include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, amyl, isoamyl, sec-amyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 1,1-dimethylbutyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, heptyl, 5-methylhexyl, 1-methylhexyl, 2,2-dimethylpentyl, 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethylpentyl, 1,2,3-trimethylbutyl, 1,1,2-trimethylbutyl, nonyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-methyloctyl, 1-, 2-, 3-, 4- or 5-ethylheptyl, 1-2- or 3-propylhexyl, decyl, 1-, 2-, 3-, 4-, 5-, 6-, 7- and 8-methylnonyl, 1-, 2-, 3-, 4-, 5- or 6-ethyloctyl, 1-, 2-, 3- or 4-propylheptyl, undecyl 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-methyldecyl, 1-, 2-, 3-, 4-, 5-, 6- or 7-ethylnonyl, 1-, 2-, 3-, 4- or 5-propyloctyl, 1-, 2- or 3-butylheptyl, 1-pentylhexyl, dodecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7-, 8-, 9- or 10-methylundecyl, 1-, 2-, 3-, 4-, 5-, 6-, 7- or 8-ethyldecyl, 1-, 2-, 3-, 4-, 5- or 6-propylnonyl, 1-, 2-, 3- or 4-butyloctyl, 1-2-pentylheptyl and the like. Examples of cyclic alkyl include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl and cyclodecyl and the like. The alkyl may optionally be substituted by any non-deleterious substituent.

In this specification "optionally substituted" means that a group may or may not be further substituted with one or more groups selected from alkyl, alkenyl, alkynyl, aryl, halo, haloalkyl, haloalkenyl, haloalkynyl, haloaryl, hydroxy, alkoxy, alkenyloxy, aryloxy, benzyloxy, haloalkoxy, haloalkenyloxy, haloaryloxy, nitro, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroaryl, nitroheterocyclyl, amino, alkylamino, dialkylamino, alkenylamino, alkynylamino, arylamino, diarylamino, benzylamino, dibenzylamino, acyl, alkenylacyl, alkynylacyl, arylacyl, acylamino, diacylamino, acyloxy, alkylsulphonyloxy, arylsulphenyloxy, heterocyclyl, heterocycloxy, heterocyclamino, haloheterocyclyl, alkylsulphenyl, arylsulphenyl, carboalkoxy, carboaryloxy, mercapto, alkylthio, benzylthio, acylthio, phosphorus-containing groups and the like. A "non-deleterious substituent" refers to any of the substituents outlined above which does not interfere with the formation of the target compound or has not interfered with the formation of the subject compound.

In the claims which follow, and in the preceding description, except where the context requires otherwise due to express language or necessary implication, the word "comprise" and variations such as "comprises" or "comprising" are used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or

addition of further features in various embodiments of the process and electrode as disclosed herein.

Claims

1. A method of electrolysing water comprising the steps of:
preparing a carbon electrode by treating a carbon material with one or more ionic liquids so as to functionalise the surface of the carbon material with ions from the ionic liquid, wherein at least one of the one or more ionic liquids has a $\Delta[\text{pka}]$ in the range of from about 10 to about 20; and
electrolysing water with the carbon electrode .
- 10 2. The method according to claim 1, wherein the step of preparing the carbon electrode comprises:
electrolysing the carbon material in an electrochemical cell wherein the carbon material forms at least part of an electroconductive electrode, and wherein the aqueous solution of the one or more ionic liquids forms the electrolyte contacting the electroconductive electrode.
3. The method according to claim 1, wherein the step of preparing the carbon electrode comprises:
mechanically agitating the carbon material with the one or more ionic liquids.
- 20 4. The method according to claim 3, wherein the mechanical agitation comprises grinding or high shear mixing.
5. The method according to any one of the preceding claims, wherein the one or more ionic liquids is provided as an aqueous solution.
6. The method according to any one of claims 1 to 5, wherein the step of preparing the carbon electrode is undertaken for a period of time sufficient to ensure that at least a part of the surface of the carbon electrode comprises one or more functional groups selected from:
30 -COOH, -CHO, -CO-, -OSO₃H, -OH, SO₃⁻, -C-F, -NC₂, NC₃⁺.
7. The method according to any one of claims 1 to 5, wherein at least one of the one or more ionic liquids comprise anions selected from the group consisting of: RSO₃⁻ or RCOO⁻, where R is an alkyl or a substituted alkyl group; (CF₃SO₃)⁻; (R-CF₂CF₂SO₃)⁻; (CF₃SO₂)N⁻; (CF₃SO₂)₃C⁻, CHF₂CF₂SO₃; (CH₃CH₂SO₄)⁻, and/or mixtures thereof.

8. The method according to any one of the preceding claims, wherein a cation of the at least one of the one or more ionic liquids comprises at least one positively charged nitrogen atom.

9. The method according to claim 8, wherein the cation comprises a nitrogen-containing aromatic ring.

10. The method according to claim 9, wherein the nitrogen-containing aromatic ring comprises an imidazolium ring.

11. The method according to claim 9, wherein the cation has the general structural formula:



wherein R^1 and R^2 are independently selected from hydrogen and a hydrocarbyl group, and wherein the hydrocarbyl group is an optionally substituted alkyl group, or an optionally substituted cycloalkyl group, or an optionally substituted heteroaryl group.

12. The method according to any one of the preceding claims, wherein the one or more ionic liquids comprises 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM][triflate]), 1 M 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIM][triflate]) or -butyl-3-methylpyrrolidinium triflate.

13. The method according to any one of the preceding claims, wherein the $\Delta[pka]$ is in the range of from about 15 to about 20.

14. The method according to any one of the preceding claims, wherein the carbon material comprises one or more of carbon black, a carbon nanofilament, a 3D carbon sieve, activated carbon, graphite, graphene, a carbide-derived carbon material, carbon nanotube, and Buckyballs.

15. The method according to any one of the preceding claims, wherein the method further comprises the step of adding a catalytic additive to the surface of the prepared carbon electrode.

16. The method according to claim 15, wherein the catalytic additive comprises a noble metal and/or a platinum group metal.

17. A method of electrolysing water comprising the steps of:

preparing a carbon electrode by treating a carbon material with one or more ionic liquids so as to functionalise the surface of the carbon material with ions from the ionic liquid, wherein at least one of the one or more ionic liquids comprises one or more anions selected from the group consisting of: RSO_3^- or RCOO^- , where R is an alkyl or a substituted alkyl group; $(\text{CF}_3\text{SO}_3)^-$; $(\text{CF}_2\text{SO}_3^-)_2$; $(\text{CF}_2\text{CF}_2\text{SO}_3^-)_2$; $(\text{CF}_3\text{SO}_2^-)_n$; $(\text{CF}_3\text{SO}_2)_3\text{C}^-$; and/or mixtures thereof; and
electrolysing water with the carbon electrode.

18. A method of preparing a carbon electrode for use in the electrolysis of water, the method comprising the step of treating a carbon material in a first cell with one or more ionic liquids so as to functionalise the surface of the carbon material with ions from at least one of the one or more ionic liquids, wherein at least one of the one or more ionic liquids has a $\Delta[\text{pka}]$ in the range of from about 10 to about 20.

19. A method of preparing a carbon electrode for use in the electrolysis of water, the method comprising the step of treating a carbon material in a first cell with one or more ionic liquids so as to functionalise the carbon, at least one of the one or more ionic liquids comprising one or more anions selected from the group consisting of: RSO_3^- or RCOO^- , where R is an alkyl or a substituted alkyl group; $(\text{CF}_3\text{SO}_3)^-$; $(\text{CF}_2\text{SO}_3^-)_2$; $(\text{CF}_2\text{CF}_2\text{SO}_3^-)_2$; $(\text{CF}_3\text{SO}_2^-)_n$; $(\text{CF}_3\text{SO}_2)_3\text{C}^-$; and/or mixtures thereof.

20. The method according to claim 18 or 19, wherein the method further includes the step of contacting the carbon electrode with water in a second cell to electrolyse the water.

21. A carbon electrode produced by a method according to any one of claims 17 to 20 when used for electrolysis.

22. An electrolysis cell for the electrolysis of water comprising the carbon electrode of claim 21.

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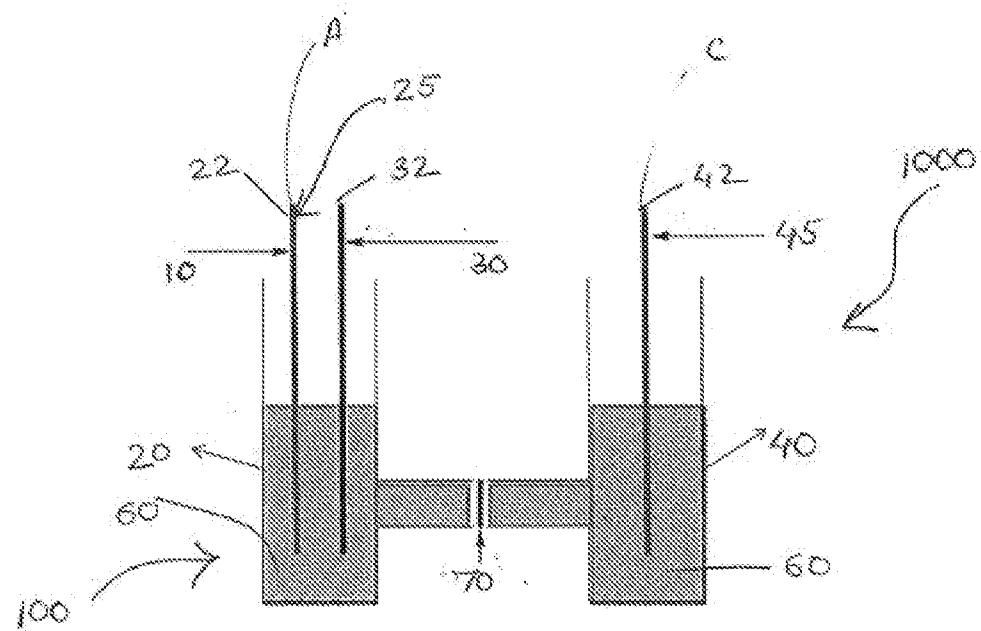


FIGURE 1

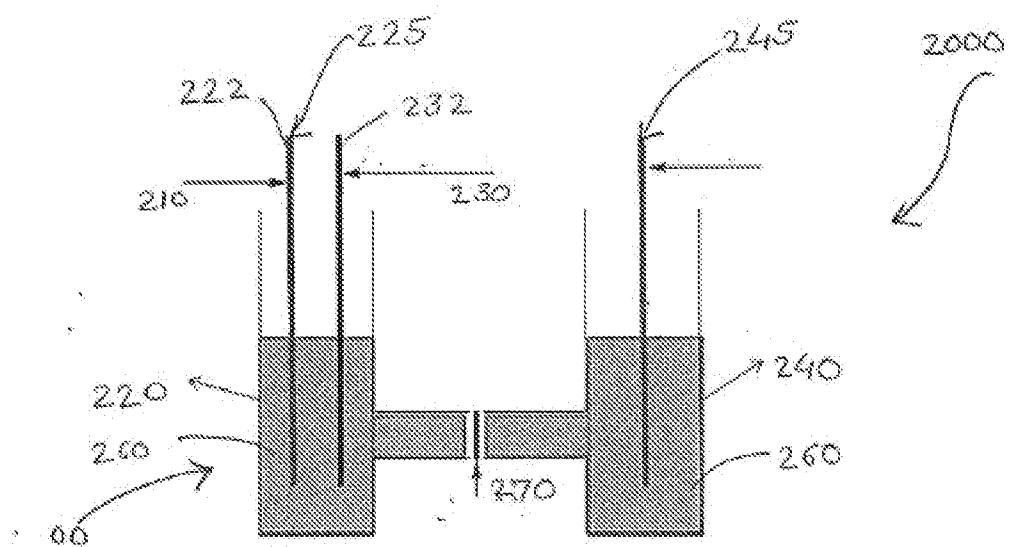


FIGURE 2

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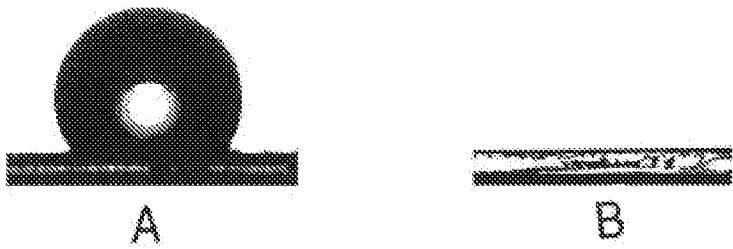


FIGURE 3

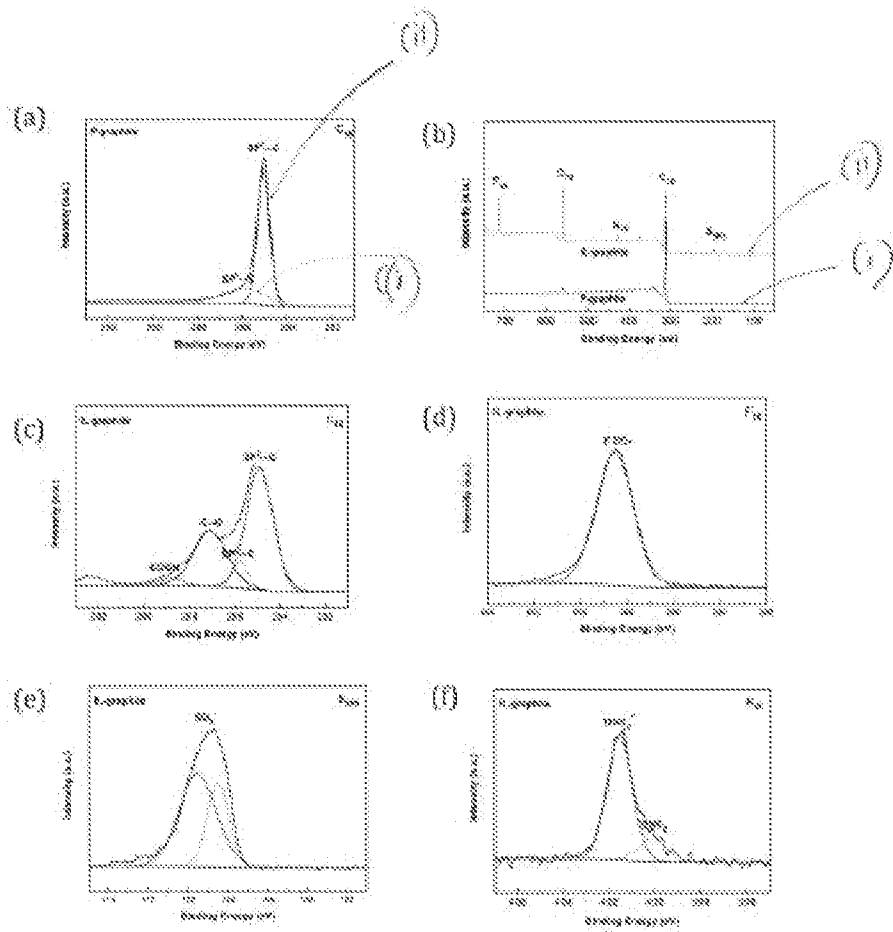


FIGURE 4

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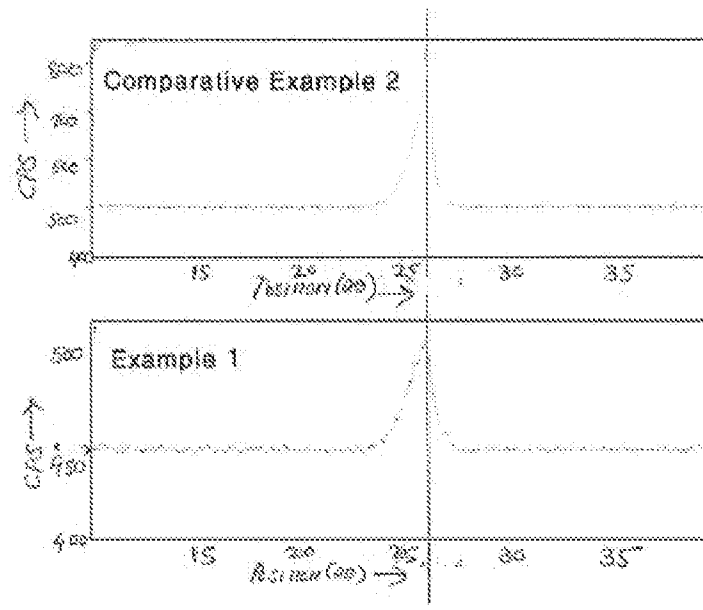


FIGURE 5

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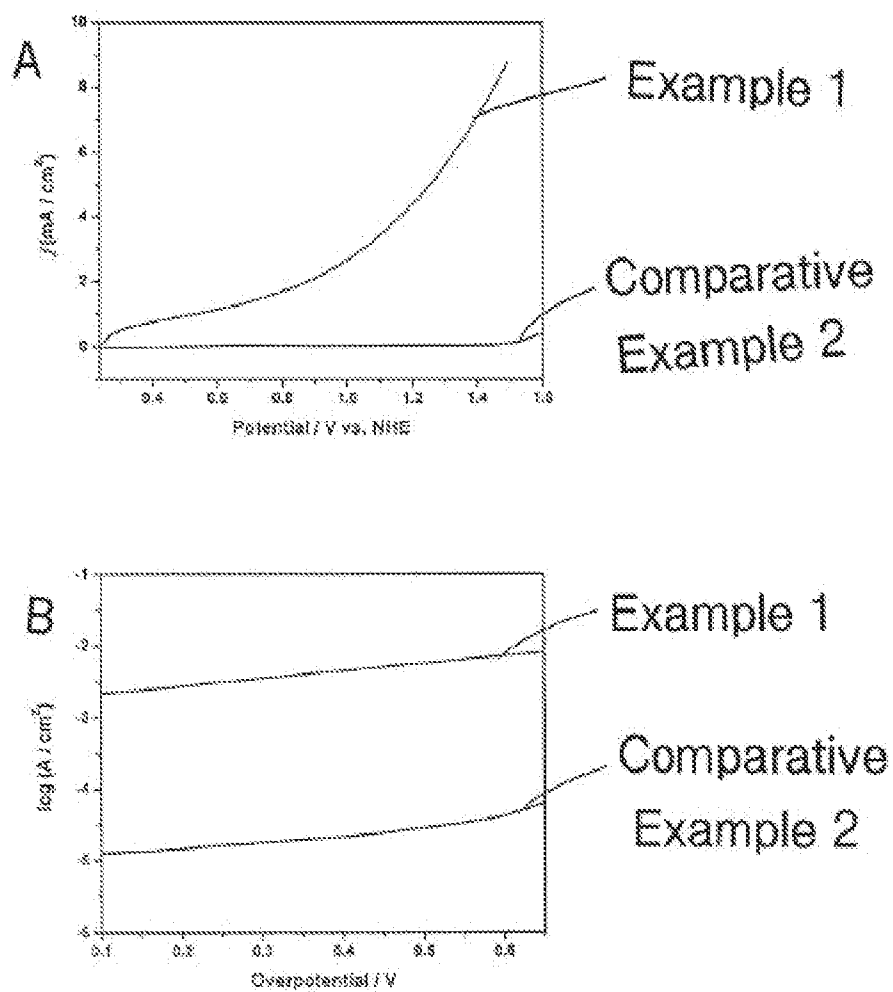


FIGURE 6

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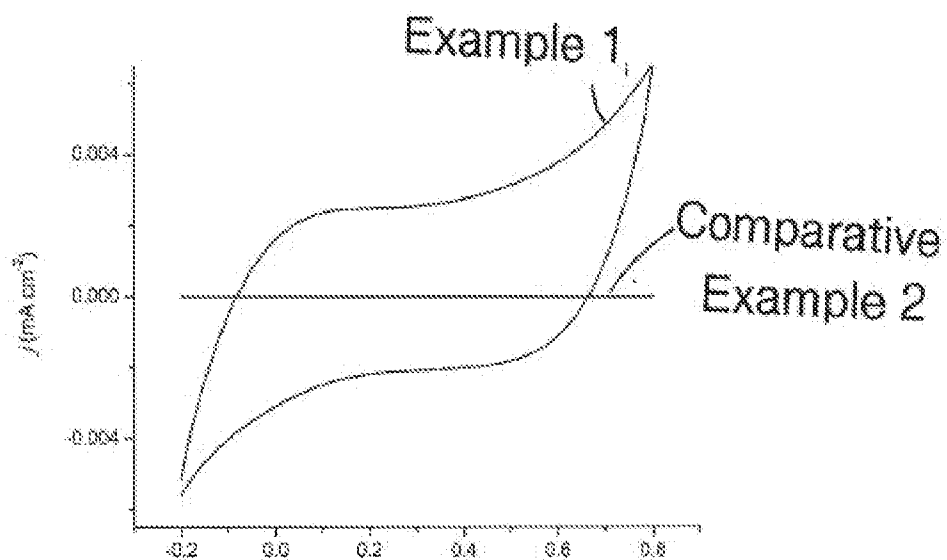


FIGURE 7

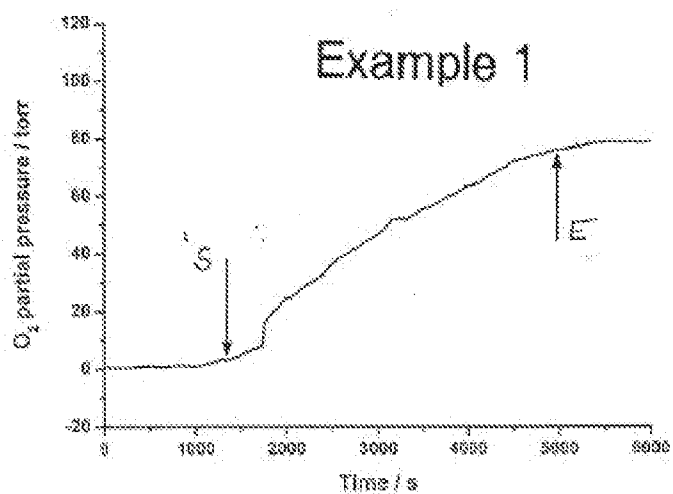


FIGURE 8

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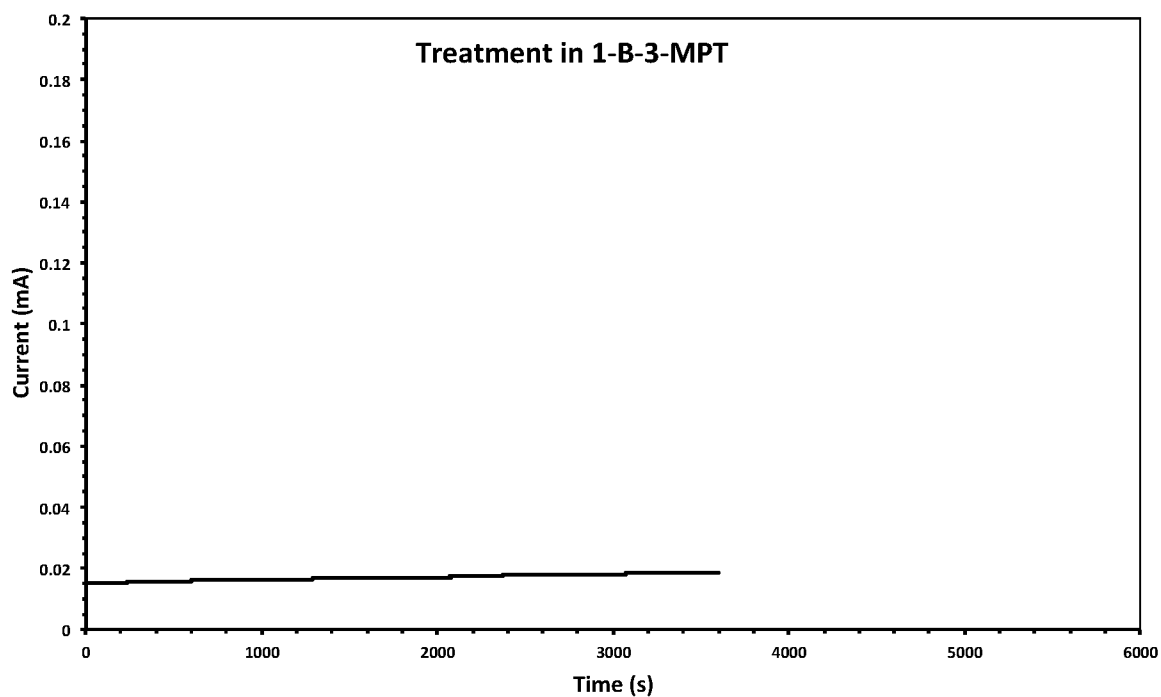


FIGURE 9

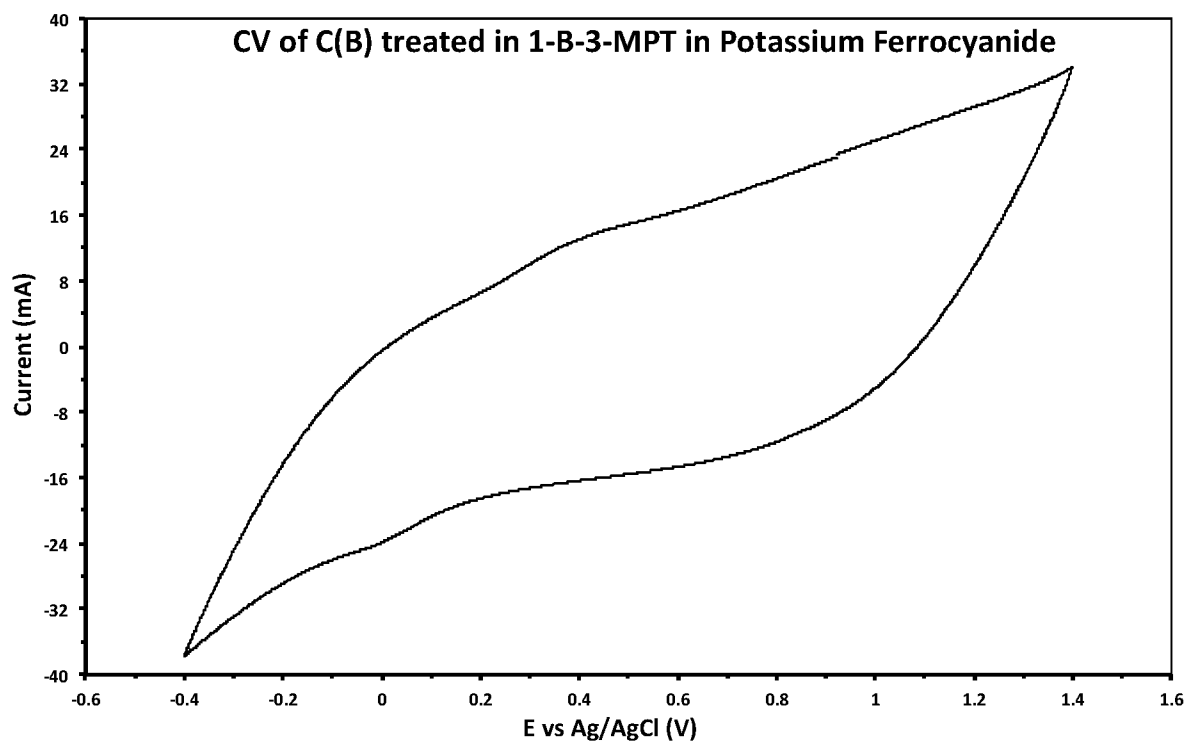


FIGURE 10

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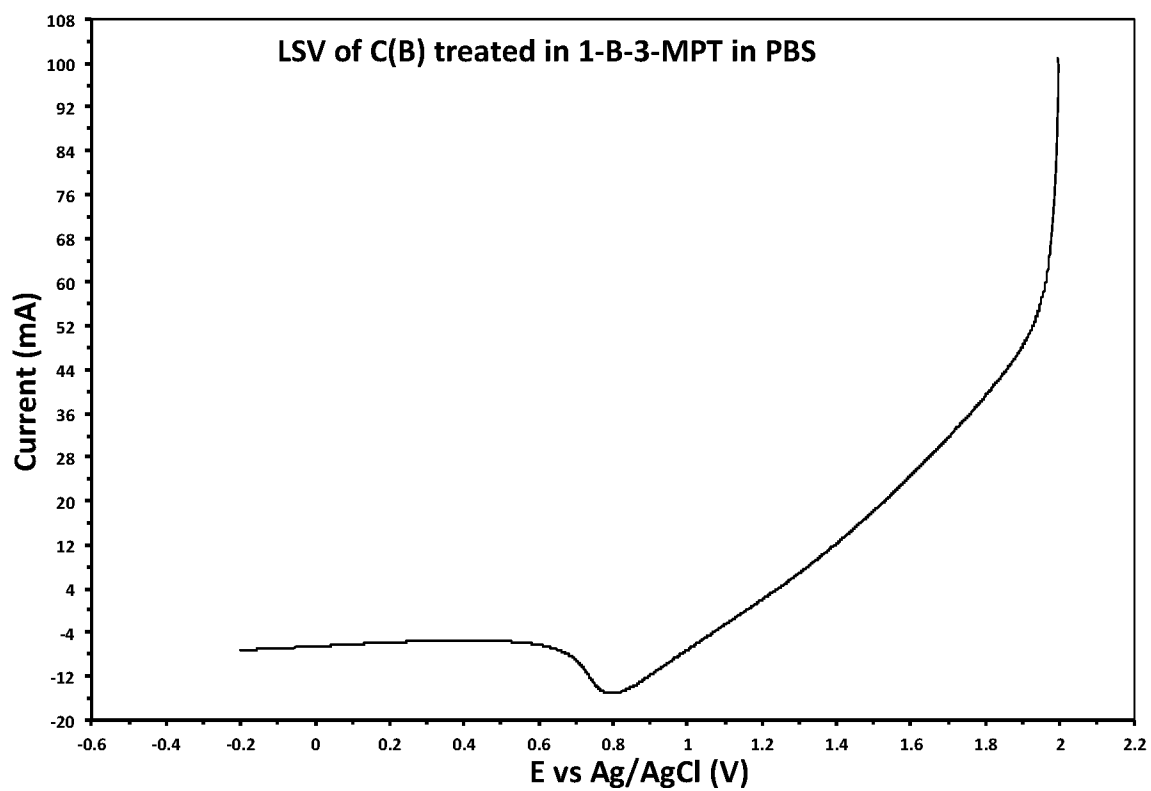


FIGURE 11

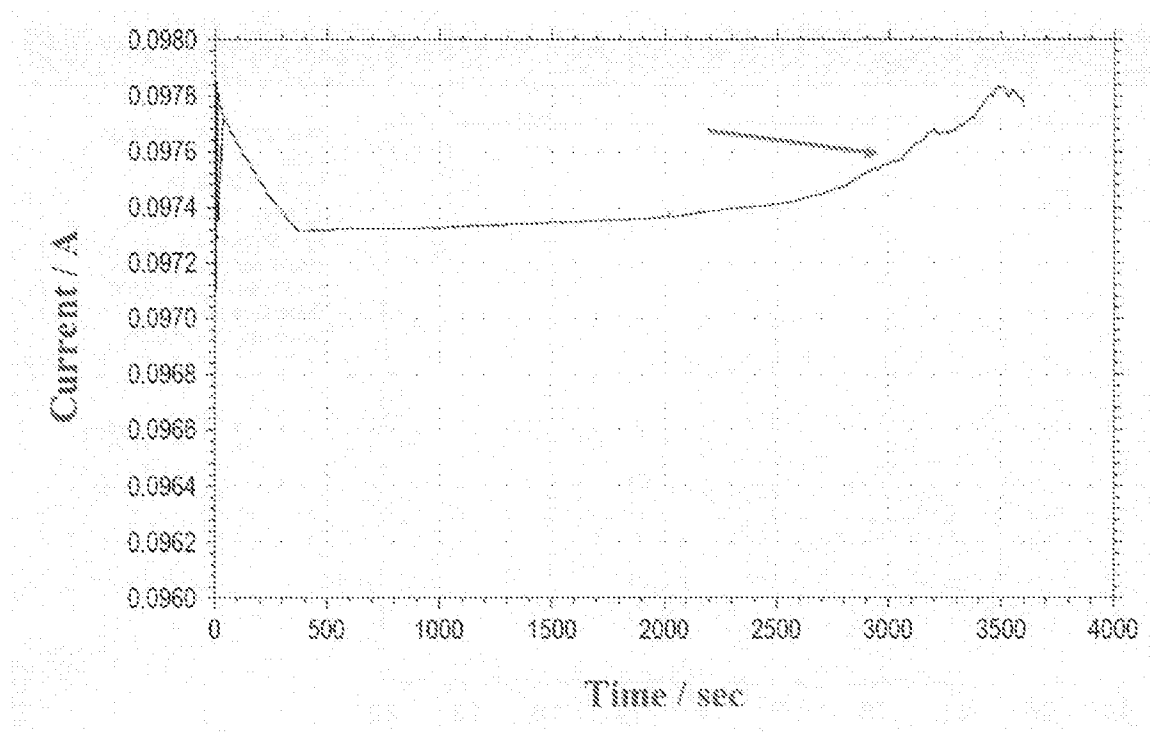


FIGURE 12A

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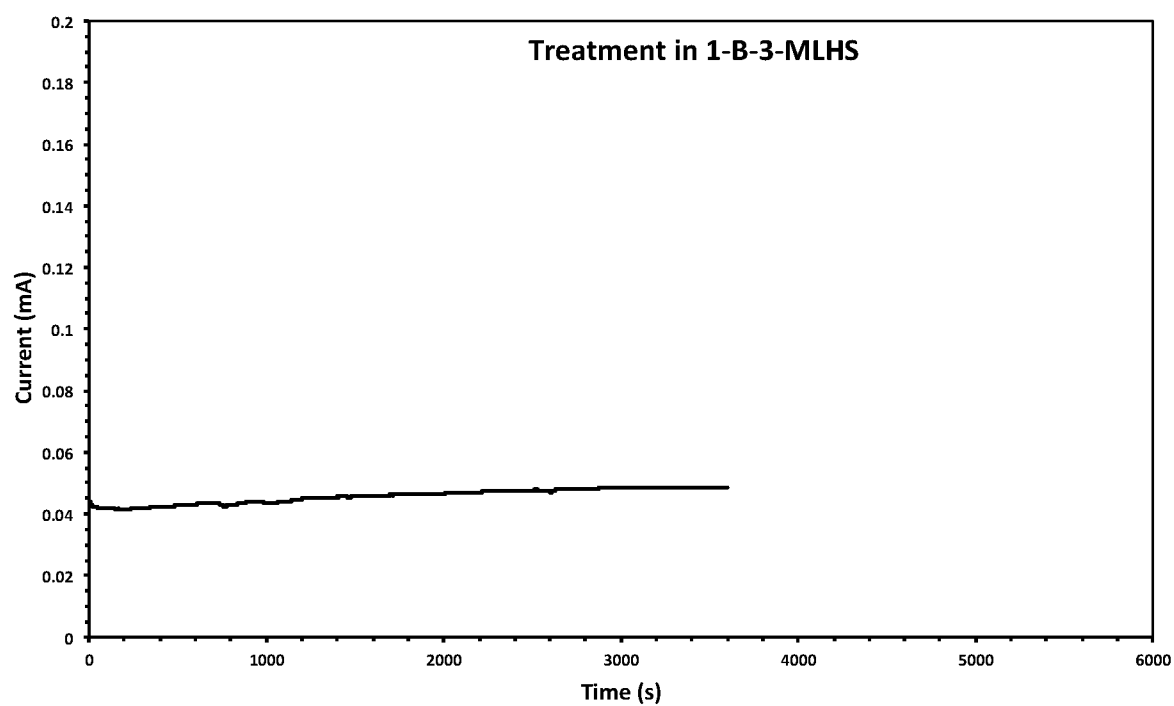


FIGURE 12B

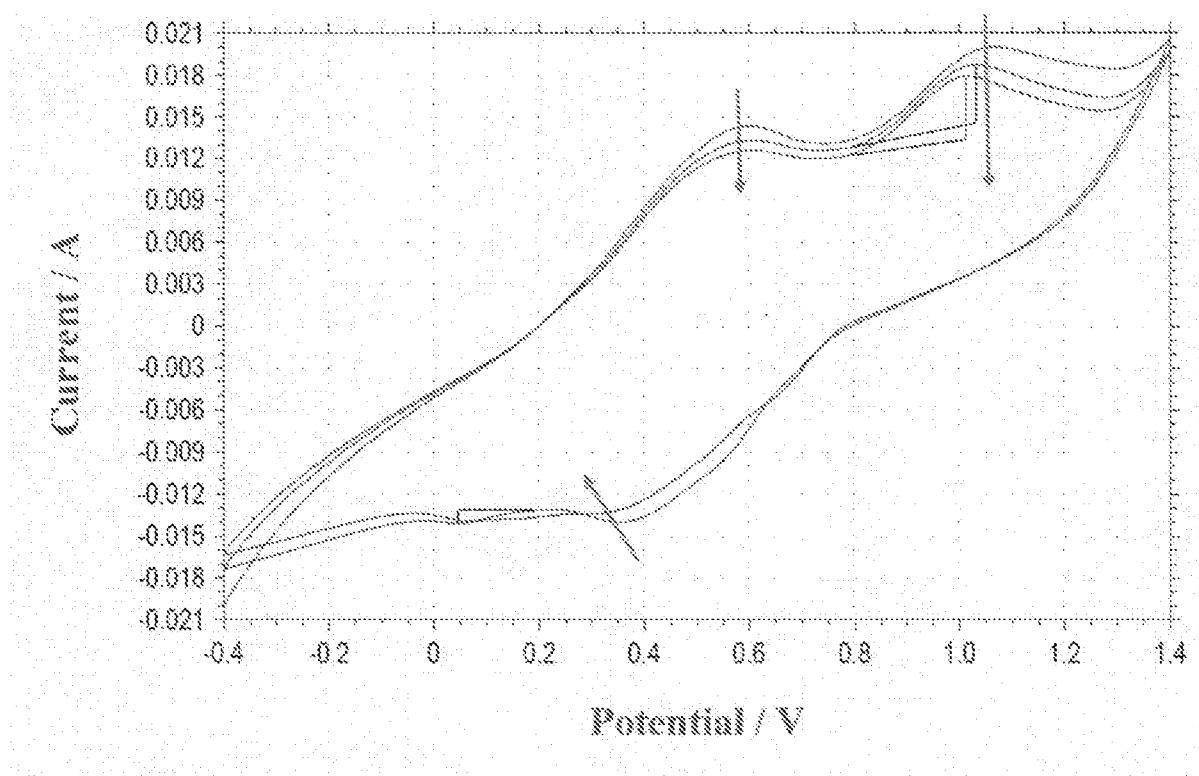


FIGURE 13A

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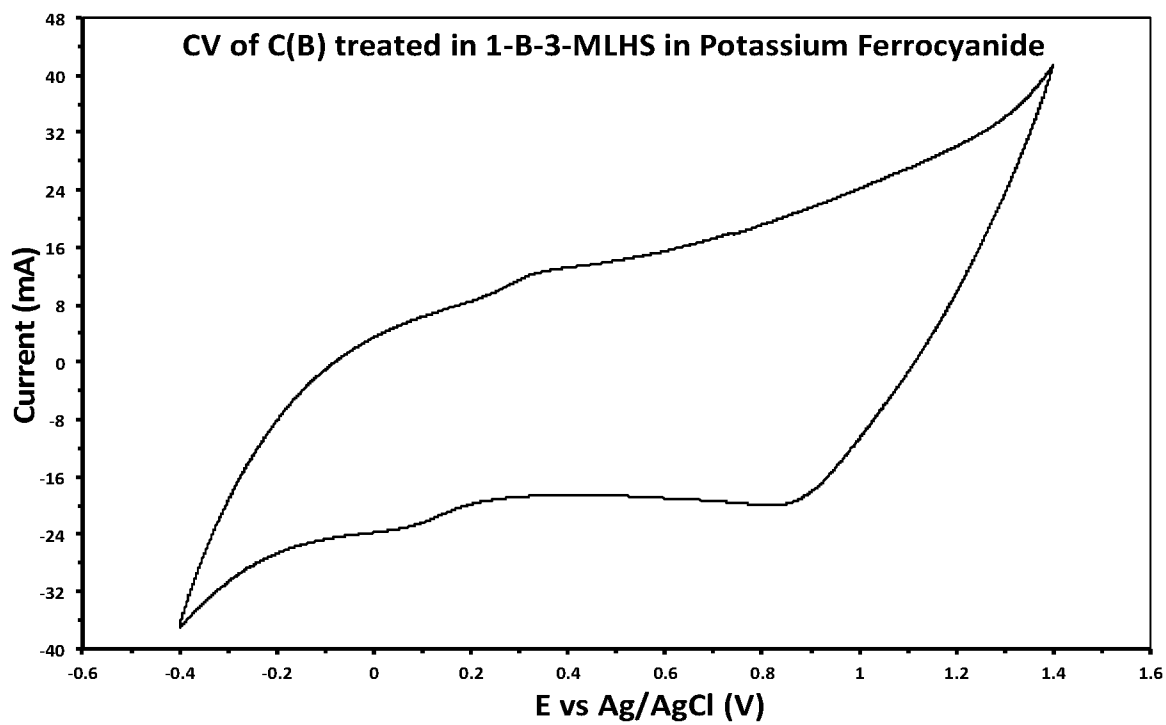


FIGURE 13B

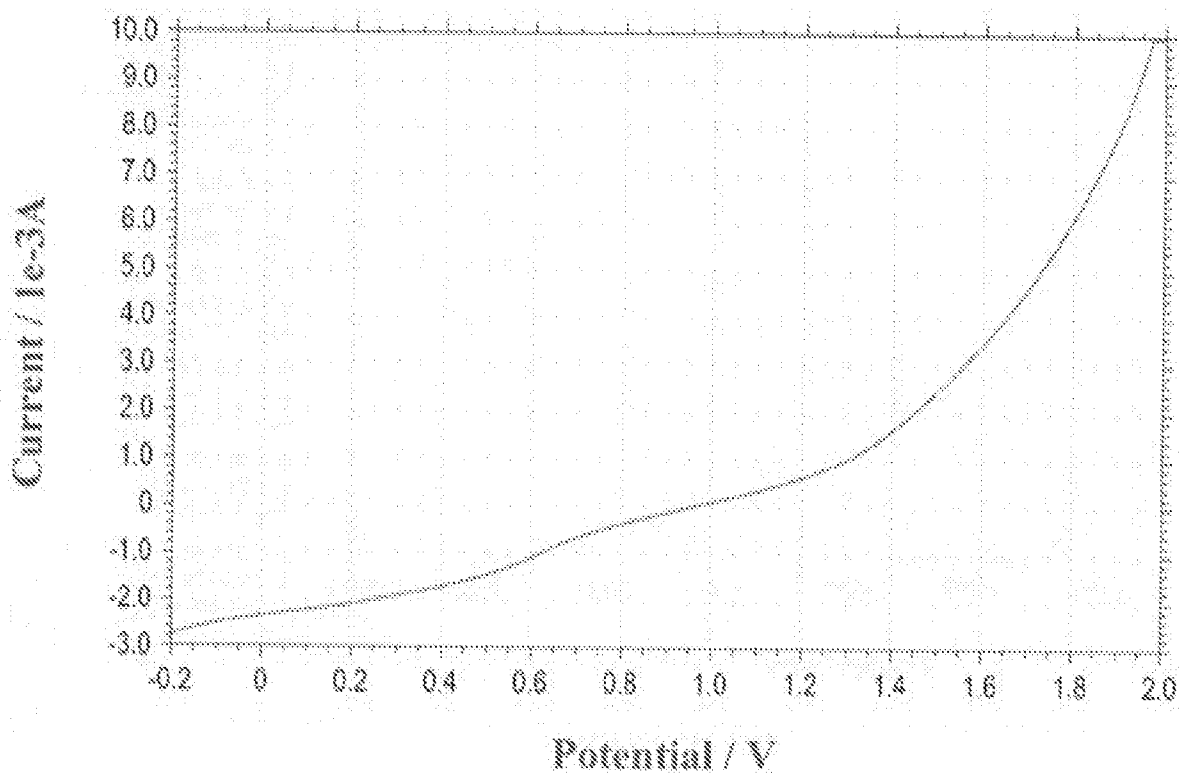


FIGURE 14A

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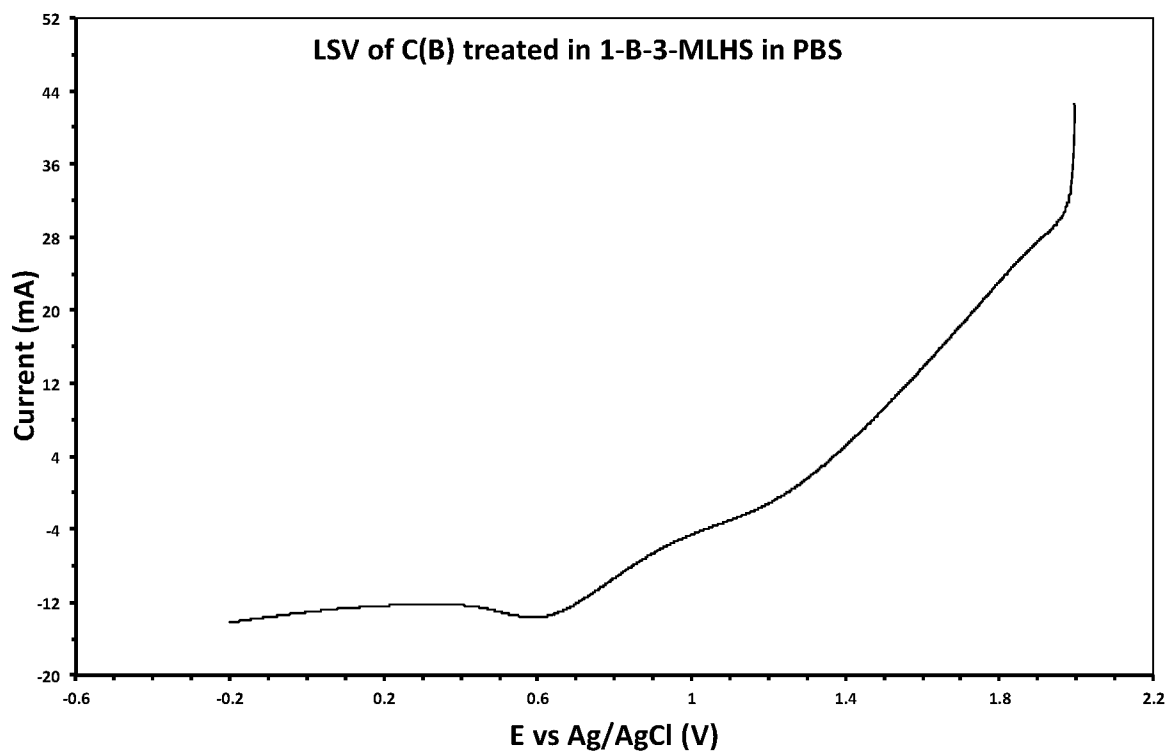


FIGURE 14B

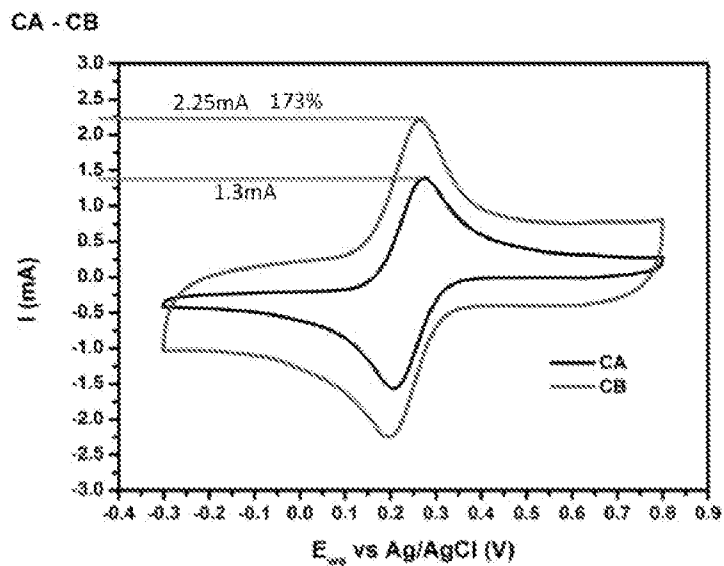


FIGURE 15

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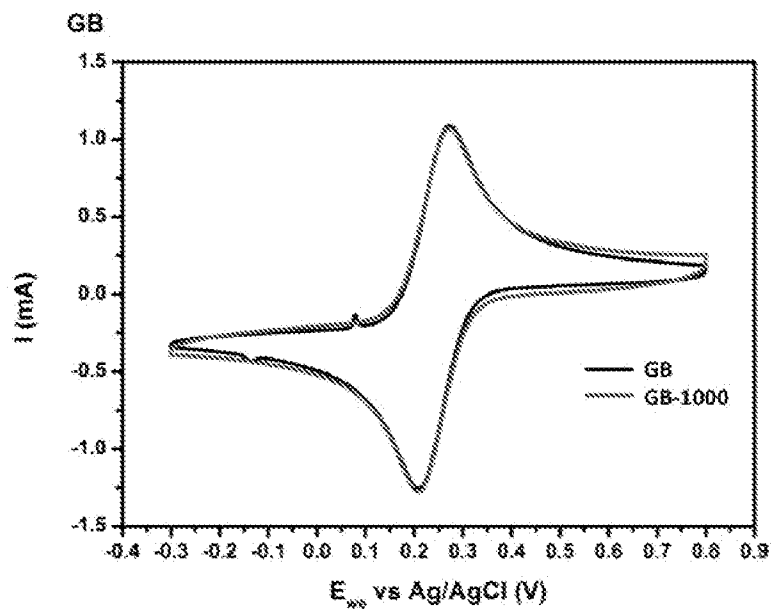


FIGURE 16

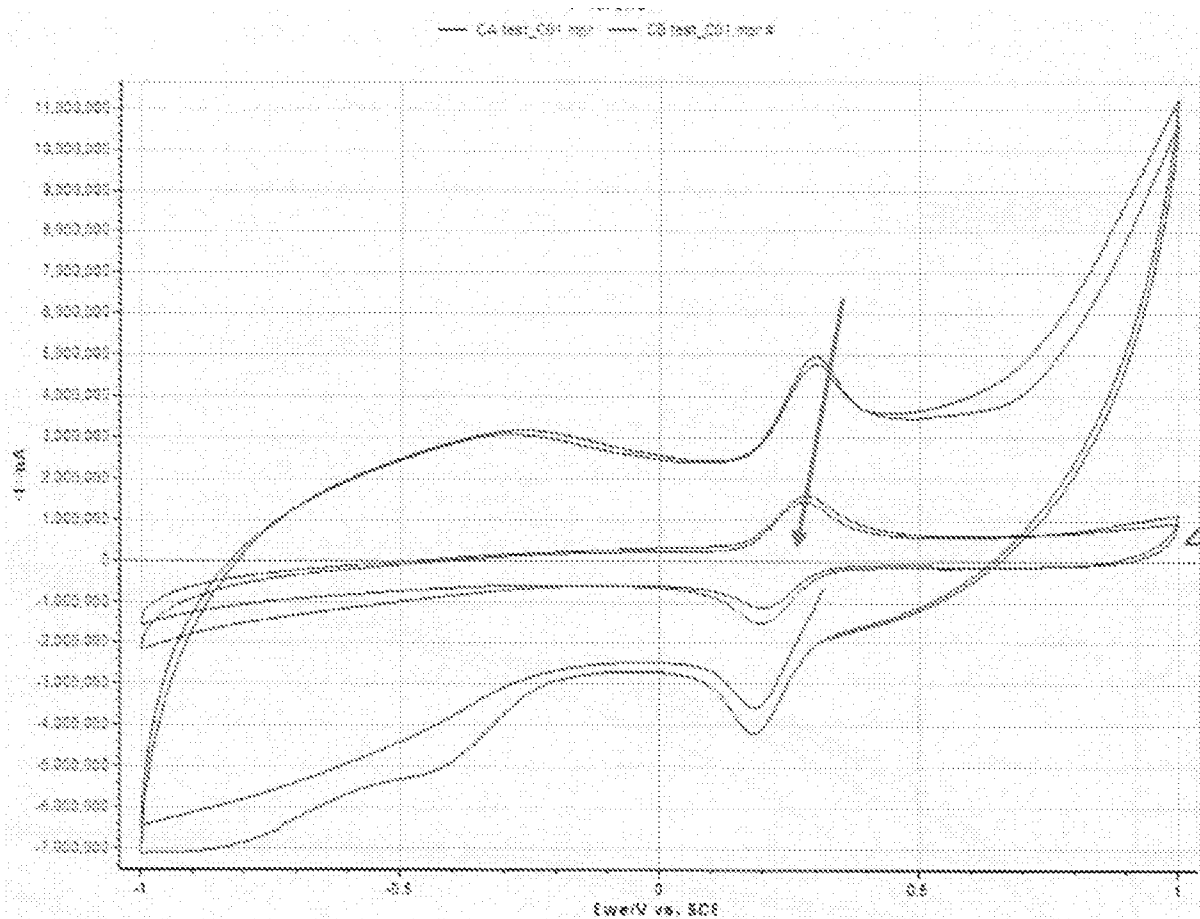


FIGURE 17

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2013/001148

A. CLASSIFICATION OF SUBJECT MATTER C25B 1/04 (2006.01) C01B 31/08 (2006.01)		
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)		
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) Derwent World Patent Index Online, CAPLUS Chemical Abstracts Online, keywords for carbon, electrodes, hydrolysis of water, ionic liquids (including those named).		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	
☒ Further documents are listed in the continuation of Box C ☒ See patent family annex		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	
Date of the actual completion of the international search 08 November 2013	Date of mailing of the international search report 11 November 2013	
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustalia.gov.au Facsimile No.: +61 2 6283 7999	Authorised officer Graeme Broxam AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262832435	

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2013/001148
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2012/0077080 A1 (LIU et. al.) 29 March 2012 Abstract, paragraphs 0037-0040, 0062-0081, Examples.	1-22
A	FONTAINE, et. al., "Ionic Liquid Viscosity Effects on the Functionalization of Electrode Material through the Electroreduction of Diazonium," <i>Langmuir</i> , Vol. 26 No. 23 (2010), pages 18542-18549. Abstract.	1-22
A	ACTIS, et. al., "Functionalization of Glassy Carbon with Diazonium Salts in Ionic Liquids," <i>Langmuir</i> , Vol. 24 (2008), pages 6327-6333. Abstract.	1-22
A	ZHANG, et. al., "Electrochemical Functionalization of Single-Walled Carbon Nanotubes in Large Quantities at a Room-Temperature Ionic Liquid Supported Three-Dimensional Network Electrode," <i>Langmuir</i> , Vol. 21 (2005), pages 4797-4800. Abstract	1-22
A	WO 2011/128213 A1 (ECOLE POLYTECHNIQUE FEDERALE DE LAUSANNE (EPFL)) 20 October 2011 Abstract	1-22
A	CN 101214954 A (NORTHEAST NORMAL UNIVERSITY) 09 July 2008 Abstract	1-22
A	Chemical Abstracts Accession No. 2012-1907924, KR 2012139563 A (EWha UNIVERSITY, INDUSTRY COLLABORATION FOUNDATION) 13 June 2012 Whole Abstract	1-22
A	US 5352339 A (KOZAWA et. al.) 04 October 1994 Abstract, example.	1-22

INTERNATIONAL SEARCH REPORT Information on patent family members		International application No. PCT/AU2013/001148	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
US 2012/0077080 A1	29 Mar 2012	None	
WO 2011/128213 A1	20 Oct 2011	EP 2558619 A1	20 Feb 2013
		US 2013068613 A1	21 Mar 2013
		WO 2011128213 A1	20 Oct 2011
CN 101214954 A	09 Jul 2008	None	
US 5352339 A	04 Oct 1994	None	
End of Annex			

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.
 Form PCT/ISA/210 (Family Annex)(July 2009)