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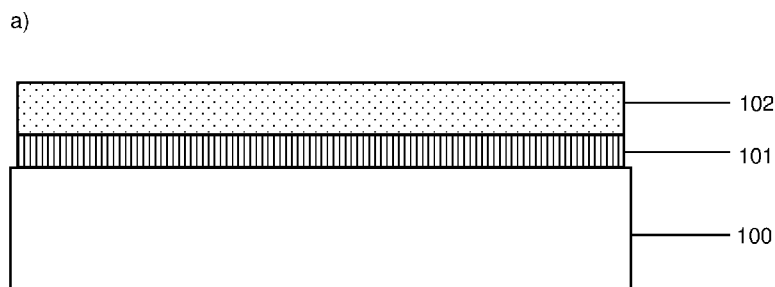
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(54) Title: CORROSION PROTECTION COATING

FIG. 1



(57) Abstract: An electrically conductive composite coating comprises a layer of an electrically conductive coating material (101) comprising a carbon-based material and an azole corrosion inhibitor; and a layer of tin or a tin alloy (102), such as tin-antimony (Sn-6wt%Sb) alloy. The coating material may include an organic binder. The coating may be used to protect a component (100) in an electrochemical device such as a fuel cell assembly, a battery, a redox flow battery, an electrolyser or a supercapacitor. The coating shows no significant sign of corrosion after 9 days in accelerated long term corrosion tests in an aggressive environment.



Corrosion Protection Coating

Field of the Invention

- 5 This invention relates to an electrically conductive composite coating for use in providing a corrosion resistant coating for components in electrochemical devices and a method of coating a component therewith.

Background to the Invention

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In the environment of fuel cells, particularly flexi-planar proton exchange membrane (PEM) fuel cells, metals, such as copper or stainless steel, appear to corrode rapidly over relatively short period of time and, as a result, the overall operational lifetime of the fuel cell is short. However, these metals have some benefits – they have high electrical and thermal conductivity, and are easy to produce complicated structures with, as is performed within the printed circuit board (PCB) industry using copper as a conductor. Corrosion is detrimental to fuel cell operation for a number of reasons: for instance it releases soluble metal ions which deactivate catalysts and impair operation of the electrolyte or the corrosion products result in an insulating barrier which prevents proper current flow.

20

Flexi-planar PEM fuel cell technology employs PCB to manufacture the fuel cells. One of the components is a planar plate commonly known as a current collector. In general, the current collector can have a metallic structure, for instance specifically shaped stainless steel or even a single metallic layer (e.g. copper) on a composite board.

25

Conditions in the fuel cell can also vary with time, for example, pH may vary from 1 to 6 (more extreme when in contact with the ion conducting membrane) as well as concentration of ions due to the dissolution of the membrane (e.g. F^- or organic species). Moreover, the change in temperature is an unavoidable process, especially during the start-up, operation and shut down of the fuel cell. Consequently, any component in the fuel cell is exposed to rather unstable conditions.

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Thus, there is a need to provide a protective coating that must withstand these unstable conditions protecting the components from corrosion. Compactness of the coating is also of utmost importance.

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In addition to that the coating must have very good electrical conductivity in order to minimise IR drop during the fuel cell operation. The U.S. Department of Energy (DoE) specifies the optimum performance of coated bipolar plates in fuel cells as having corrosion resistance with corrosion current less than $1 \mu\text{Acm}^{-2}$ for the cathode and anode side and a conductivity of greater than 100 Scm^{-1} . Furthermore, they set the contact resistance goal for PEM fuel cell applications at lower than $10 \text{ m}\Omega \text{ cm}^2$ at 140 N/cm^2 compaction pressure for 2015 (Wind J, Späh R, Kaiser W, Böhm G. Metallic bipolar plates for PEM fuel cells. J Power Sources 2002;105:256-260, the contents of which is herein incorporated by reference in its entirety). These requirements pose a rather large demand on the performance of the coating.

Thus, there is a need for an improved coating for substrates and components used in fuel cells. Similarly, there is need for improved corrosion protection coatings in, for example, batteries, redox flow batteries, electrolyzers and supercapacitors.

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Summary of the Invention

The corrosion potential of fuel cells resulting from the reactant materials used can be significantly reduced by applying appropriate coatings to components of the fuel cell. The invention provides a coating that can be applied to a substrate to reduce the corrosion rate to a minimum and maintain high electrical conduction and low contact resistance.

Accordingly, in a first aspect, the invention provides an electrically conductive composite coating comprising:

- 25 a layer comprising an electrically conductive coating material comprising a carbon-based material and an azole-containing corrosion inhibitor; and
- a layer comprising tin.

The following discussion of the layer comprising an electrically conductive coating material, the carbon-based material, the azole-containing corrosion inhibitor and the layer comprising tin in relation to the first aspect of the invention apply *mutatis mutandis* to the second to the eighth aspects of the invention which follow.

The carbon-based material may comprise carbon black, coal, charcoal, graphite, carbon fibres, carbon nanotubes or graphene or mixtures thereof.

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- The electrically conductive coating material may further comprise an organic binder. Preferably the organic binder comprises organic monomeric and/or oligomeric polymer precursor compounds. The electrically conductive coating material may comprise a carbon ink comprising the carbon-based material and the organic binder, so that the carbon-based material and organic binder are components of the carbon ink. The electrically conductive coating material may comprise about 50 wt% to about 90 wt% of the carbon-based material, preferably about 70 to about 90 wt% or about 80 wt% of the carbon-based material.
- The azole-containing corrosion inhibitor may be benzotriazole, 2-mercaptobenzimidazole, 5-phenyl tetrazole, *bis*[4-amino-5-hydroxy-1,2,4-triazol-3-yl]methane or *bis*[4-amino-5-hydroxy-1,2,4-triazol-3-yl]butane, or mixtures thereof, preferably the azole-containing corrosion inhibitor is benzotriazole. The azole-containing corrosion inhibitor may be present in the electrically conductive coating material in an amount of about 10 wt% or less of the amount of carbon-based material and organic binder, preferably about 5 wt% or less, preferably about 1 wt%. When the carbon-based material and organic binder are provided as components in a carbon ink, the azole-containing corrosion inhibitor may be present in the electrically conductive coating material in an amount of about 10 wt% or less of the amount of carbon ink, preferably about 5 wt% or less, preferably about 1 wt%.
- The layer comprising tin may comprise tin metal and/or tin alloy, for example, a tin-nickel alloy, a tin-antimony alloy, a tin-indium alloy, a tin-gallium alloy, a tin-indium-antimony alloy or tin-nickel-antimony alloy or mixtures thereof.
- The layer comprising an electrically conductive coating material may be about 1 to about 100 μm thick, preferably about 1 to about 50 μm thick, preferably about 1 to about 40 μm thick, about 5 to about 30 μm thick, about 5 to about 25 μm thick, about 10 to about 20 μm thick, or about 15 to about 20 μm thick. The layer comprising tin may be about 1 to about 20 μm thick, preferably about 2 to about 15 μm thick, or about 5 to about 10 μm thick.
- The electrically conductive composite coating may have an area specific electrical resistance of less than about 10 $\text{m}\Omega\text{ cm}^2$.
- The electrically conductive composite coating material as described herein may be for use in coating a substrate, for example, a metallic substrate, preferably a copper, iron, titanium, aluminium, nickel or stainless steel substrate. The substrate may be a

component in an electrochemical device, such as a fuel cell assembly, a battery, a redox flow battery, an electrolyser or a supercapacitor.

In a second aspect, the invention provides a coated article comprising;

- 5 a substrate as described herein; and
 an electrically conducting composite coating comprising a layer comprising an electrically conductive coating material comprising a carbon-based material and an azole-containing corrosion inhibitor, and a layer comprising tin.
- 10 The coated article may comprise an electrically conducting composite coating comprising:
 two or more layers comprising an electrically conductive coating material comprising a carbon-based material and an azole-containing corrosion inhibitor; and
 two or more layers comprising tin.
- 15 The electrically conducting composite coating may comprise any of the features discussed in relation to the first aspect of the invention.

The substrate may be a metallic substrate, preferably a copper, iron, titanium, aluminium, nickel or stainless steel substrate. The substrate may, in particular, be a component for
20 an electrochemical device, such as a fuel cell assembly, a battery, a redox flow battery, an electrolyser or a supercapacitor.

In a third aspect, the invention provides an electrically conductive coating material comprising:

- 25 a carbon ink as described herein; and
 an azole-containing corrosion inhibitor.

In a fourth aspect, the invention provides an electrically conductive coating material comprising:

- 30 a carbon-based material as described herein; and
 an azole-containing corrosion inhibitor as described herein, wherein the azole-containing corrosion inhibitor is benzotriazole, 2-mercaptobenzimidazole, 5-phenyl tetrazole, *bis*[4-amino-5-hydroxy-1,2,4-triazol-3-yl]methane or *bis*[4-amino-5-hydroxy-1,2,4-triazol-3-yl]butane, or mixtures thereof, preferably the azole-containing corrosion
35 inhibitor is benzotriazole.

In a fifth aspect, the invention provides a process for coating a substrate with an electrically conductive composite coating, the process comprising:

- providing a substrate;
- depositing a layer comprising tin on a surface of the substrate; and
- 5 depositing a layer comprising an electrically conductive coating material comprising a carbon-based material and an azole-containing corrosion inhibitor as a layer on said surface of the substrate.

The process may further comprise:

- 10 depositing a further layer comprising tin on a surface of the coated substrate;
 - depositing a further layer comprising an electrically conductive coating material comprising a carbon-based material and an azole-containing corrosion inhibitor on said surface of the substrate.
- 15 The process may further comprise the step of heat treating the coated substrate after deposition of the layer comprising an electrically conductive coating material, preferably wherein the heat treatment comprises heating to at least about 100°C, at least about 125°C or at least about 150°C, for at least about 30 minutes, at least about 45 minutes or at least about 1 hour.

- 20 Depositing a layer comprising tin may comprise electrodeposition of tin and/or a tin alloy onto the substrate. Depositing a layer comprising an electrically conductive coating material may comprise screen printing the electrically conductive coating material as a layer on top of the layer comprising tin.

- 25 In a sixth aspect, the invention provides a coated article obtainable by or obtained by the process for coating a substrate with an electrically conductive coating as described herein.

- In a seventh aspect, the invention provides an electrochemical device, such as a fuel cell assembly, a battery, a redox flow battery, an electrolyser or a supercapacitor comprising a
30 coated article as described herein.

In an eighth aspect, the invention provides use of an electrically conductive composite coating comprising:

- 35 a layer comprising an electrically conductive coating material comprising a carbon-based material and an azole-containing corrosion inhibitor; and a layer comprising tin; as a corrosion resistant coating for a component in an electrochemical device.

Embodiments described herein in relation to the first and second aspects of the invention apply *mutatis mutandis* to the third to the eighth aspects of the invention.

Description of Figures

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Figure 1 shows cross sections of (a) a coated article according to the invention comprising a substrate (100) and an electrically conductive composite coating comprising a layer comprising tin (101), provided on at least a surface of the substrate, and a layer comprising an electrically conductive coating material (102), provided on the layer comprising tin; and
10 (b) a coated article according to the invention comprising a substrate (100), two layers comprising an electrically conductive coating material (102), and two layers comprising tin (101).

Figure 2 shows the corrosion current for (a) an electrically conductive coating material layer (solid curve) and an electrically conductive composite coating (dashed curve) and (b) a layer
15 comprising tin. The DoE target of 1000 nA cm^{-2} for corrosion of bipolar plates is shown as a dashed line.

Figure 3 shows the behaviour of electrically conductive coating material layer in a corrosive environment as part of an accelerated long-term corrosion test. The temperature of the solution was cycled between room temperature (R.T.) and 80°C every 24 h. The DoE target
20 of 1000 nA cm^{-2} for corrosion of bipolar plates is shown as a dashed line.

Figure 4 shows the behaviour of an electrically conductive composite coating in a corrosive medium as part of an accelerated long-term corrosion test. The temperature of the solution was cycled between R.T. and 80°C every 2 h. The DoE target of 1000 nA cm^{-2} for corrosion
of bipolar plates is shown as a dashed line.

Figure 5 shows the behaviour of a multi-layered electrically conductive composite coating in a corrosive medium as part of an accelerated long-term corrosion test. The coating is composed of four layers: a layer comprising tin as a first layer, an electrically conductive coating material layer as a second layer, a layer comprising a Sn-Sb alloy as a third layer and an electrically conductive coating material layer as a fourth layer. The DoE target of
25 1000 nA cm^{-2} for corrosion of bipolar plates is shown as a dashed line.
30

Detailed Description of the Invention

The corrosion potential of fuel cells, batteries, redox flow batteries, electrolyzers and
35 supercapacitors resulting from the reactant materials used can be significantly reduced by applying appropriate coatings to components of a fuel cell, battery, redox flow battery, electrolyser or supercapacitor. Accordingly, in a first aspect, the invention provides

electrically conductive composite coating comprising: a layer comprising an electrically conductive coating material comprising a carbon-based material and an azole-containing corrosion inhibitor; and a layer comprising tin. This electrically conductive coating composite may be applied to a surface of a substrate to provide a corrosion resistant layer, whilst maintaining conductivity of the substrate. This composite coating may be applied to components in a fuel cell. Using this approach it has been found that the stability of the components is significantly increased whilst at the same time maintaining a low contact resistance.

10 The coating composites and materials of the present invention may be applied to a substrate to provide a corrosion resistant protective coating. The substrate may be a metallic substrate in need of corrosion protection, preferably a copper, iron, titanium, aluminium, nickel or stainless steel substrate. The substrate may be a component in a fuel cell, battery, redox flow battery, electrolyser or supercapacitor where the conditions may be harsh and
15 variable during the operation of the device with a lifetime of, for example, 5,000 hours or more. For example, the substrate may be a planar plate in the flexi-planar proton exchange membrane (PEM) fuel cell, as described in patent number WO 2013/164639, the contents of which is herein incorporated by reference in its entirety. The flexi-planar technology employs printed circuit boards (PCB) to manufacture the fuel cells. An exemplary
20 component to which the composite coating or coating material of the invention may be applied is a planar plate, commonly known as a current collector.

The coating composites and materials of the present invention provide may be applied to the entirety of the substrate or a part of the substrate. A substrate may have multiple faces.
25 The coating may be applied to coat a single face entirely or more than one of the faces entirely. Alternatively, all of the faces of a substrate may be coated entirely so that the entirety of the substrate is coated.

The present invention relates to electrically conductive composite coatings and coating
30 materials. These coating composites and materials may be used to coat components in a fuel cell, battery, redox flow battery, electrolyser or supercapacitor. Good electrical conductivity is beneficial to minimise voltage drop (IR-drop) during the fuel cell operation. Electrical conductivity is a measure of a material's ability to conduct an electric current. Resistivity is the reciprocal of conductivity and quantifies how strongly a given material
35 opposes the flow of electric current. A low resistivity indicates a material that readily allows the movement of electric charge. The area specific electrical resistance of the electrically conductive composite coating (including the contact resistance) may be less than about 10

mΩ cm², wherein the area specific electrical resistance is a product of the resistivity and the thickness of the coating. For example, the electrically conductive composite may have a thickness of about 100 μm, in which case, the coating may have a resistivity of less than about 1 Ωcm. The electrically conductive composite coating may be less than about 100 μm thick, preferably about 5 to about 50 μm, about 5 to about 40 μm, about 10 to about 30 μm, about 10 to about 20 μm. The layer comprising an electrically conductive coating material may be about 1 to about 50 μm thick, preferably about 5 to about 25 μm thick, preferably, about 10 to about 20 μm thick. The layer comprising tin may be about 1 to about 20 μm thick, preferably about 5 to about 10 μm thick.

10

The resistivity (in Ωcm) of the coating composites and materials of the present invention can be calculated from the contact area (in cm²), sample thickness (cm), and resistance (Ω) of a sample according to the following equation:

$$\text{Resistivity} = \text{Resistance} \times \frac{\text{contact area}}{\text{sample thickness}}$$

Resistance is determined by applying a current source to the sample, measuring the resultant voltage, and calculating resistance with Ohm's Law ($V = IR$). The resistance of the sample may be measured at pressures of about 140 N/cm² (about 1.4 MPa), which is in accordance with the DoE target for the pressure exerted in the fuel cells. The resistance may then be used to calculate the resistivity, according to the above equation using the contact area and thickness of the sample, and then the area specific electrical resistance, by determining the product of the resistivity and the sample thickness. Measuring of the resistance and resistivity of a coated substrate is described in L. Landis *et al.*, Making Better Fuel Cells: Through-Plane Resistivity Measurement of Graphite-Filled Bipolar Plates, 2002, Keithly Instruments, Inc. White Paper (<https://www.keithley.co.uk/data?asset=10382>), the contents of which is herein incorporated by reference in its entirety.

A carbon-based material of the present invention is a material comprising an elemental form of carbon. An elemental form of carbon is carbon which is at least 90% pure carbon, preferably at least 92%, at least 94%, at least 96%, or at least 98% pure carbon, calculated as a weight percentage. Examples of elemental form of carbon include graphite, graphene, carbon nanotubes, carbon nanofibres, charcoal, coal and carbon black, or mixtures thereof. A carbon-based material of the present invention may consist essentially of an elemental form of carbon. Accordingly, a carbon-based material may consist essentially of graphite, graphene, carbon nanotubes, carbon nanofibres, charcoal, coal and carbon black or mixtures thereof and the material may, therefore, be at least at least 90wt% carbon, preferably at least 92wt%, at least 94wt%, at least 96wt%, or at least 98wt% carbon. A

carbon-based material of the present invention may comprise particles of the elemental carbon material.

5 An electrically conductive coating material of the present invention may further comprise an organic binder. An organic binder serves as a vehicle to hold the particles of the elemental carbon and may be formed from resins or organic monomeric and/or oligomeric polymer precursor compounds. Examples of such resins and precursor compounds include acrylics, alkyds, cellulosic derivatives, rubber resins, ketones, maleics, formaldehydes, phenolics, epoxies, fumarics, hydrocarbons, isocyanate free polyurethanes, poly vinyl butyral,
10 polyamides, shellac, and polycarbonates.

An oligomeric polymer precursor compound may refer to an organic compound comprising 2 or more monomeric repeat units, preferably 2 to 5. A polymer may consist of multiple repeat units, preferably at least 6, and may be a homopolymer, copolymer, or a mixture
15 thereof.

A carbon-based material may be provided as a component in a carbon ink. A carbon ink is a material comprising a carbon-based material and an organic binder. A carbon ink as described herein may preferably be a conductive carbon ink. A carbon ink as described
20 herein is in line with the general understanding in the art. Generally, a carbon ink is an ink that may be easily screen printed and comprises carbon as a pigment along with a binder. A carbon ink may have a dynamic viscosity of between about 2.9 poise and about 7 poise, when calculated at 20°C and 1 atmosphere. Therefore, a carbon ink may be a viscous material. Dynamic viscosity may be measured by a viscometer, calibrated to the viscosity
25 of distilled water at 20°C and 1 atmosphere (0.01 poise).

When a carbon-based material is provided as a component in a carbon ink, the organic binder comprises the resins that are also used to form carbon inks. Exemplary carbon inks include PCB1 Sunchemical ink 2sp, PCB3 Sunchemical ink 2sp revisited and PCB4
30 Sunchemical ink (last) 2sp.

Azole-containing corrosion inhibitors of the present invention are compounds that contain one or more substituted or unsubstituted, fused or non-fused azole ring. An azole is a class of five-membered nitrogen-containing heterocyclic ring compounds containing at least one
35 other non-carbon ring atom of either nitrogen, sulfur, or oxygen. Exemplary azoles include pyrrole, pyrazole, imidazole, triazole, tetrazole, pentazole, oxazole, isoxazole, thiazole, and isothiazole, optionally substituted with one or more of halo, aliphatic (e.g. alkyl, alkenyl or

alkynyl), cycloaliphatic, heterocycloaliphatic, aryl, heteroaryl, alkoxy, amino, hydroxy, carboxyl, acetyl, nitro, cyano, sulfonyl and thiol or combinations thereof. These azole rings may be fused with another ring to form ring system comprising two or more rings. For example, an azole may be fused with an aryl ring (for example, a phenyl ring). The azole-
5 containing corrosion inhibitors of the present invention are chemical compounds that decreases the corrosion rate of a material. Exemplary azole-containing corrosion inhibitors include benzotriazole, 2-mercaptobenzimidazole, 5-phenyl tetrazole, *bis*[4-amino-5-hydroxy-1,2,4-triazol-3-yl]methane or *bis*[4-amino-5-hydroxy-1,2,4-triazol-3-yl]butane, or mixtures thereof, preferably the azole-containing corrosion inhibitor is benzotriazole.

10

The azole-containing corrosion inhibitor may be present in the electrically conductive coating material at an amount of about 10 weight percent (wt%) or less of the amount of carbon-based material and organic binder, preferably about 5 wt% or less, preferably about 1 wt%. That is to say, the wt% of the corrosion inhibitor is calculated as a percentage of
15 the total weight of carbon-based material and organic binder in the electrically conductive coating material.

An electrically conductive coating material of the present invention may consist essentially of a carbon-based material, organic binder and azole-containing corrosion inhibitor.

20

An electrically conductive coating material of the present invention may comprise about 50 weight percent (wt%) to about 90 wt% of the carbon-based material, preferably about 60 to about 90 wt%, preferably about 70 to about 90 wt%, about 75 to about 85 wt% or about 80 wt% of the carbon-based material. The remaining part of the electrically conductive coating
25 material may comprise (or consist essentially of) organic binder and azole-containing corrosion inhibitor.

Tin, as used herein, refers to a material comprising tin as a pure metal and/or as a tin-alloy. For example, a tin alloy may be a binary tin alloy or a ternary tin alloy comprising tin and
30 one or more of nickel, antimony, indium or gallium. A tin-alloy is preferably a tin-nickel alloy, a tin-antimony alloy, a tin-indium alloy, a tin-gallium alloy, a tin-indium-antimony alloy or tin-nickel-antimony alloy or mixtures thereof. A layer comprising tin, as described herein, may consist essentially of tin metal and/or a tin alloy as described herein.

35 In another aspect, the invention provides a process for coating a substrate with an electrically conductive composite coating, the process comprising:

providing a substrate as described herein;

depositing a layer comprising tin on a surface of the substrate; and

depositing a layer comprising an electrically conductive coating material as described herein on said surface of the substrate.

- 5 Figure 1 (a) shows a cross section a substrate that has been coated according to a process for coating a substrate as described herein. This coated article formed by this process comprises the substrate (100) and an electrically conductive composite coating comprising the layer comprising tin (101) and the layer comprising an electrically conductive coating material (102).

10

- The steps of depositing a layer comprising tin and depositing a layer comprising an electrically conductive coating material may be repeated one or more times to form a coated substrate comprising an electrically conductive composite coating comprising at least two layers comprising tin and/or at least two layers comprising an electrically conductive coating material. Figure 1 (b) shows a coated article formed by a process for coating a substrate as described herein and further comprising the further repeated steps depositing a layer comprising tin and depositing a layer comprising an electrically conductive coating material. This coated article comprises a substrate (100) and an electrically conductive composite coating comprising two layers comprising an electrically conductive coating material (102), and two layers comprising tin (101).

20

- A coated article, as described herein, comprises a substrate and an electrically conductive coating material comprising a layer comprising an electrically conductive coating material and a layer comprising tin. The layer comprising tin may be provided on (preferably directly in contact with) a surface of the substrate. The layer comprising an electrically conductive coating material may then be provided on (preferably directly in contact with) the layer comprising tin so that the layer comprising tin is interposed between the substrate and the layer comprising an electrically conductive coating material, as shown in figure 1 (a). A coated article comprising a substrate and an electrically conductive coating material comprising more than one layer (for example, two layers) comprising an electrically conductive coating material and more than one layer (for example, two layers) comprising tin may be structured as alternating layer, for example, as shown in figure 1 (b).

30

- After deposition of the layer comprising an electrically conductive coating material, the process may comprise the step of heat treating the coated substrate, preferably wherein the heat treatment comprises heating to at least about 100°C, at least about 125°C or at

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least about 150°C, for at least about 30 minutes, at least about 45 minutes or at least about 1 hour.

5 The process may comprise the step of washing the substrate prior to deposition of the layer comprising tin. Washing the substrate may comprise soaking the substrate in water and/or an organic solvent and/or rinsing the substrate with water and/or an organic solvent, preferably washing the substrate comprises soaking the substrate in an organic solvent optionally followed by rinsing the substrate with water. Any commercially available standard laboratory solvent may be used to wash the substrate. Preferably the organic solvent is
10 acetone. After washing, the substrate may be dried.

The layer comprising tin is then deposited on a surface of the substrate. The layer comprising tin may comprise tin as a metal and/or as a tin-alloy. A tin-alloy is preferably a tin-nickel alloy, a tin-antimony alloy, a tin-indium alloy, a tin-gallium alloy, a tin-indium-
15 antimony alloy or tin-nickel-antimony alloy or mixtures thereof. The layer comprising tin may be deposited onto the substrate by electrodeposition. Electrodeposition of the layer comprising tin may be carried out by preparing an aqueous solution of the tin and/or tin alloy, placing the tin solution into contact with the surface of the substrate and applying a current through the tin solution. An aqueous solution of the tin and/or tin alloy may be
20 prepared by dissolving tin salts (for example, tin sulfate or tin chloride) and optionally salts of one or more of nickel, antimony, indium or gallium (for example, sulfates or chlorides) in an aqueous solution. After the electrodeposition of the layer comprising tin is completed, the tin-coated substrate may be washed with (either soaked in or rinsed with) water (preferably deionised water) and the remaining tin on the coating may be wiped off with soft
25 tissue until the clean and metallic coating is observed.

The layer comprising an electrically conductive coating material as described herein is then deposited on said surface of the substrate. Deposition of the electrically conductive coating material may be carried out by screen printing. The electrically conductive coating material
30 may be prepared by combining the carbon-based material, the organic binder and the corrosion inhibitor until a homogeneous mixture is achieved. This coating material may then be screen printed on to the tin-coated substrate using a screen printer. This results in the deposition of a layer comprising an electrically conductive coating material on top of the layer comprising tin.

35 Post-treatment once the coating is prepared is not required. The coated substrate is ready to be used.

Examples

Reference is now made to the following examples, which illustrate the invention in a non-limiting fashion.

5

EXAMPLE 1

The substrate to which the electrically conductive composite coating is to be applied is copper-cladded composite board and a cross section of the possible coating arrangements is shown in Figure 1.

10

Cleaning of the substrate:

The substrate was soaked in acetone for 5 minutes and then rinsed with deionised water (DI) and dried with a soft tissue.

15

Electrodeposition of tin onto the substrate:

A tin plating solution for electrodeposition was prepared comprising commercially available Sn bath, pH 0.5 – 1 or 0.45 M $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.45 M $\text{K}_4\text{P}_2\text{O}_7$. The pH was adjusted to 6 with aqueous ammonia solution. The bath temperature during the plating was maintained at 35°C.

Plating baths for tin alloys comprises of Sn metal ions with complexing agents (such as chloride or sulfate), with additives and with other metal ions to be alloyed in, for instance Sb, Ga, In or Ni. An example of a plating bath for Sn-6 wt%Sb consists of:

- 5 g/L SnSO_4
- 5 g/L $\text{Sb}(\text{SO}_4)_3$
- 100 g/L concentrated H_2SO_4
- 1 g/L PEG 5800 or 2 g/L PEG 3000
- 2 g/L Coumarin (7-Diethylamino-4-methylcoumarin)
- 33 g/L $\text{K}_4\text{P}_2\text{O}_7$

The pH of the above plating bath is around 1 and the bath temperature was maintained at 28°C.

30

The substrate was copper-cladded composite board and was placed in the tin bath and a current density of -10 mA cm^{-2} was applied for 600 seconds in order to deposit coating with thickness of about 5 μm , calculated from Faradays law assuming 100% current efficiency and 100% dense Sn deposited.

35

After the plating was finished, the tin-coated substrate was rinsed with dionised water and the residual tin on the coating was wiped out with soft tissue until the clean tin coating was observed.

5 Deposition of electrically conductive coating material using a semi-automatic screen printer:

A Sunchemical ink was mixed with 1 wt% Benzotriazole until a homogeneous mixture was achieved. To deposit a layer of the electrically conductive coating material, a semi-automatic screen printer was used with blades passing over the surface to be coated four times to
10 achieve a thickness of about 20-25 μm .

Heat treatment:

After the electrically conductive coating material was screen printed, the whole coated article was placed in a preheated oven at about 150°C for 1 hour. After 1 hour, the coated substrate
15 was kept inside the oven and allowed to cool to room temperature.

EXAMPLE 2

A study was conducted for various coatings and the coatings were tested in an aggressive
20 environment as part of an accelerated corrosion test. A 1 M Na_2SO_4 solution adjusted to pH 3 with sulphuric acid at 80°C was selected for these tests. The solution was not deaerated. The potential was stepped to +0.6 V vs. SHE and held at this potential for 1 h. The coatings were continuously immersed in the solution and electrochemical tests, mimicking operation of PEM fuel cell, were conducted. Such tests allowed selection of the
25 best possible coating.

Coating Selection:

Three major groups of coatings were tested: the electrically conductive coating material only (max 35 μm thick), a tin layer coating only (max. about 5 μm thick), and electrically
30 conductive composite coating comprising a layer comprising an electrically conductive coating material (max. about 35 μm thick), and a layer comprising tin (max. about 5 μm thick). These coatings were prepared according to the methods set out in Example 1.

Figure 2 shows results for the three types of coatings tested. It is clear that the corrosion
35 current was related to the type of coating. The electrically conductive coating material (solid curve, figure 2 (a)) showed localised dissolution within 1 hour – large current spikes were observed. This suggests that the coating was degrading with time.

The tin coating on the other hand showed completely different behavior: a large dissolution peak was first observed (dotted curve in figure 2 (b)) and after about 2000 seconds the current rapidly decreased to very low values, then crossed the “time” axis and became cathodic although still increasing to more positive current. This was clear evidence that almost half of the coating dissolved and some oxide layer was formed within 2000 seconds. After this time the dissolution rate was negligible but still increasing with time. Extended accelerated corrosion test showed that after 3.5 days of temperature cycling between room temperature (R.T.) and 80°C, the corrosion current increased from nanoamperes per cm² to large values, way above the DoE target.

The electrically conductive composite coating (dashed curve in figure 2 (a)), showed the optimum corrosion current: no current spikes present (no local degradation) and the trend of the curve was decreasing with time.

The study of coatings’ corrosion was further extended - the time of the testing was much longer and the temperature was cycled between R.T. and 80°C holding at each temperature for a fixed period of time – either 24 or 2 hours – until the failure of the coating was observed (the corrosion current density exceeded DoE target, which is less than about 1 $\mu\text{A cm}^{-2}$). As before, the test solution used was 1 M Na₂SO₄, pH 3. Solutions were not deaerated. The potential was stepped to +0.6 V vs. SHE and held at this potential for 24 h at each temperature.

As mentioned above, the metallic coating lasted only 3.5 days under accelerated corrosion test upon cycling the temperature. For the electrically conductive coating material layer on the other hand, no initial dissolution/oxide formation was recorded but an increasing corrosion current density was seen with time, see Figure 3. After 120 hours, failure was observed.

By combining the metallic and organic coating together to form an electrically conductive composite coating and performing the accelerated long-term corrosion test (cycling the temperature every 2 hours in order to expose the coating to even more harsh conditions), the results were surprisingly good, see Figure 4. After 9 days, there was no significant sign of corrosion increase and the magnitude of the corrosion current was much below the DoE target (DoE target is shown in figure 4). The negative corrosion current density indicates cathodic behaviour of the coating, i.e. the coating is not corroding at this potential.

Combination of metallic and organic coating shows a synergistic effect – the coating did not fail within 9 days of accelerated corrosion test – such test would be equivalent to almost 1 year of normal PEM fuel cell operation, whereas single-layered coating deteriorated rather quickly under such conditions.

5

EXAMPLE 3 – multilayer coating

In this example, a composite coating comprising two layers comprising an electrically conductive coating material and two layers comprising tin was prepared for much better performance. The composite coating is shown in figure 1 (b). It comprises electrodeposited Sn layer followed by the screen printing of an electrically conductive coating material layer, followed by electrodeposition of Sn-6wt%Sb alloy and final electrically conductive coating material layer. The overall thickness was max. about 40 μm .

15 Corrosion test

The performance of the coating was again tested in the accelerating corrosion test in solution comprising of 1 M Na_2SO_4 pH 3 and the temperature was cycled between R.T. and 80°C every 2 h until the corrosion current exceeded the DoE target. The solution was not deaerated. The potential was stepped to +0.6 V vs. SHE and held at this potential for 1 h. The behaviour of the coating is shown in figure 5 – corrosion current density showed a very good behaviour for over 18 days. Although the current density was increased with time, the DoE target was not exceeded.

Clearly, such coating's configuration showed a very good corrosion barrier simultaneously maintaining low contact resistance. In fact, the contact resistance of such family of coatings was below about 1 $\text{m}\Omega\cdot\text{cm}^2$.

Embodiments of the invention have been described by way of example only. It will be appreciated that variations of the described embodiments may be made which are still within the scope of the invention.

Claims

1. An electrochemical device comprising a coated article comprising;
a substrate; and
5 an electrically conductive composite coating comprising a layer comprising an electrically conductive coating material comprising a carbon-based material and an azole-containing corrosion inhibitor; and a layer comprising tin.
2. The electrochemical device of claim 1, wherein the electrically conductive composite
10 coating comprises:
two or more layers comprising an electrically conductive coating material comprising a carbon-based material and an azole-containing corrosion inhibitor;
and
two or more layers comprising tin.
- 15 3. The electrochemical device of claim 1 or 2, wherein the electrically conductive coating material comprises a carbon-based material comprising carbon black, coal, charcoal, graphite, carbon fibres, carbon nanotubes or graphene or mixtures thereof.
- 20 4. The electrochemical device of any preceding claim, wherein the electrically conductive coating material further comprises an organic binder, preferably wherein the organic binder comprises organic monomeric and/or oligomeric polymer precursor compounds.
- 25 5. The electrochemical device of claim 4, wherein the electrically conductive coating material comprises a carbon ink comprising the carbon-based material and the organic binder.
6. The electrochemical device of any preceding claim, wherein the electrically
30 conductive coating material comprises about 50 wt% to about 90 wt% of the carbon-based material, preferably about 70 to about 90 wt% or about 80 wt% of the carbon-based material.
7. The electrochemical device of any preceding claim, wherein the azole-containing corrosion inhibitor is benzotriazole, 2-mercaptobenzimidazole, 5-phenyl tetrazole, *bis*[4-amino-5-hydroxy-1,2,4-triazol-3-yl]methane or *bis*[4-amino-5-hydroxy-1,2,4-triazol-3-yl]butane, or mixtures thereof, preferably the azole-containing corrosion inhibitor is benzotriazole.
- 35

8. The electrochemical device of any of claims 4 to 7, wherein the azole-containing corrosion inhibitor is present in the electrically conductive coating material in an amount of about 10 wt% or less of the amount of carbon-based material and organic binder,
5 preferably about 5 wt% or less, preferably about 1 wt%.
9. The electrochemical device of any preceding claim, wherein the layer comprising tin comprises tin metal and/or tin alloys (preferably a tin-nickel alloy, a tin-antimony alloy, a tin-indium alloy, a tin-gallium alloy, a tin-indium-antimony alloy or tin-nickel-antimony
10 alloy or mixtures thereof).
10. The electrochemical device of any preceding claim, wherein:
a) the layer comprising an electrically conductive coating material is about 1 to about 50 μm thick, preferably about 5 to about 25 μm thick, preferably,
15 about 10 to about 20 μm thick; and/or
b) the layer comprising tin is about 1 to about 20 μm thick, preferably about 5 to about 10 μm thick.
11. The electrochemical device of any preceding claim, wherein the electrically
20 conductive composite coating has an area specific electrical resistance of less than about 10 $\text{m}\Omega\text{ cm}^2$.
12. The electrochemical device of any preceding claim, wherein the substrate is a metallic substrate, preferably a copper, iron, titanium, aluminium, nickel or stainless steel
25 substrate.
13. The electrochemical device according to any preceding claim, wherein the substrate is a component in a fuel cell assembly, a battery, a redox flow battery, an electrolyser or a supercapacitor.
30
14. A coated article for an electrochemical device comprising;
a substrate; and
an electrically conductive composite coating comprising a layer comprising
an electrically conductive coating material comprising a carbon-based material and an
35 azole-containing corrosion inhibitor; and a layer comprising tin.

15. The coated article of claim 14, comprising an electrically conductive composite coating comprising:

two or more layers comprising an electrically conductive coating material comprising a carbon-based material and an azole-containing corrosion inhibitor; and

5 two or more layers comprising tin.

16. A process for providing a coated article for an electrochemical device, the process comprising:

providing a substrate;

10 depositing a layer comprising tin on a surface of the substrate; and

depositing a layer comprising an electrically conductive coating material comprising a carbon-based material and an azole-containing corrosion inhibitor as a layer on said surface of the substrate.

15 17. The process of claim 16, further comprising:

depositing a further layer comprising tin on a surface of the coated substrate;

20 depositing a further layer comprising an electrically conductive coating material comprising a carbon-based material and an azole-containing corrosion inhibitor on said surface of the substrate.

18. Use of an electrically conductive composite coating comprising:

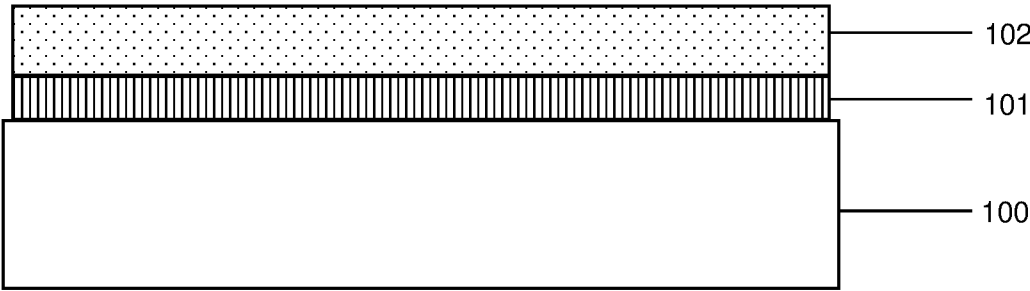
25 a layer comprising an electrically conductive coating material comprising a carbon-based material and an azole-containing corrosion inhibitor; and a layer comprising tin;

as a corrosion resistant coating for a component in an electrochemical device.

30

FIG. 1

a)



b)

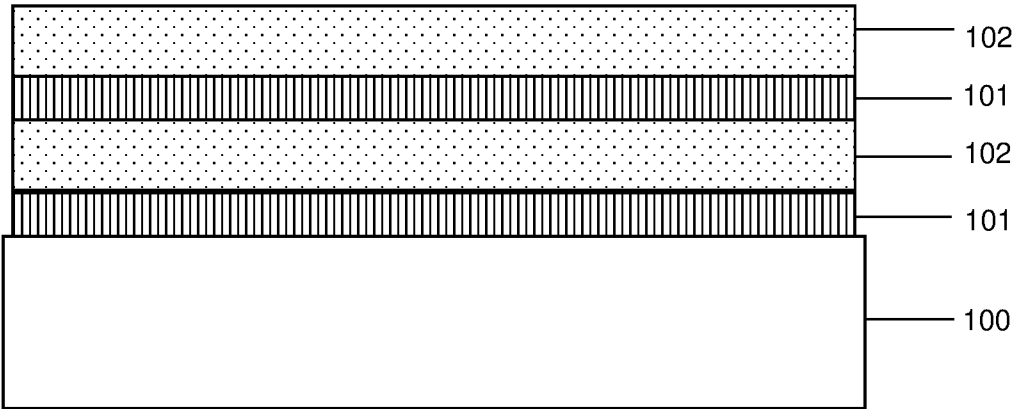
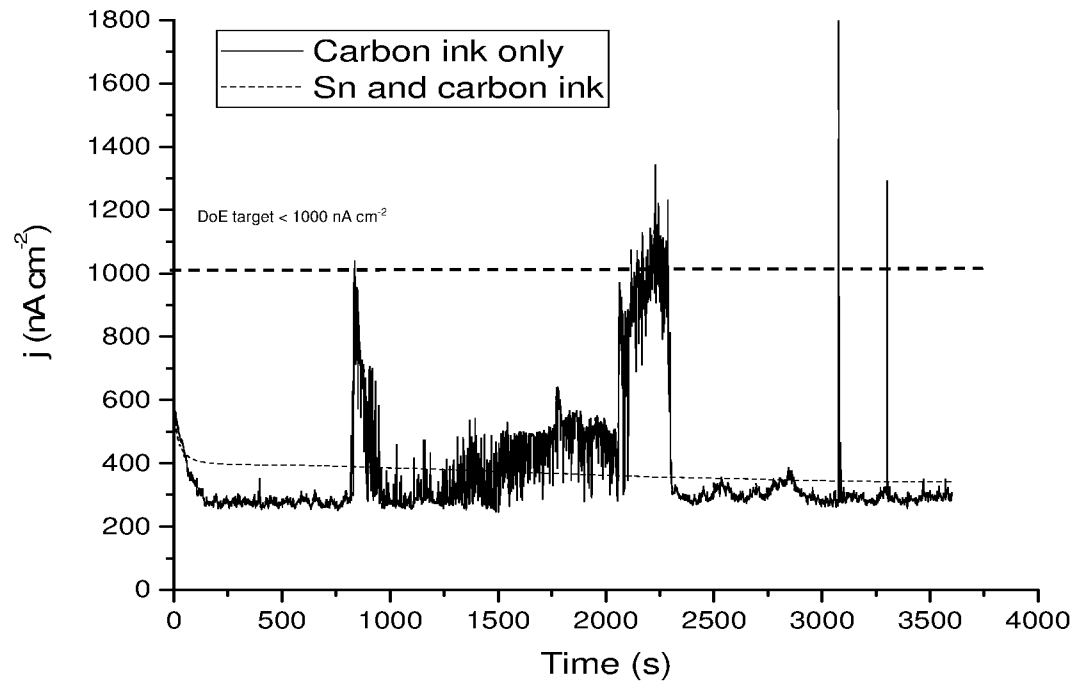


FIG. 2

a)



b)

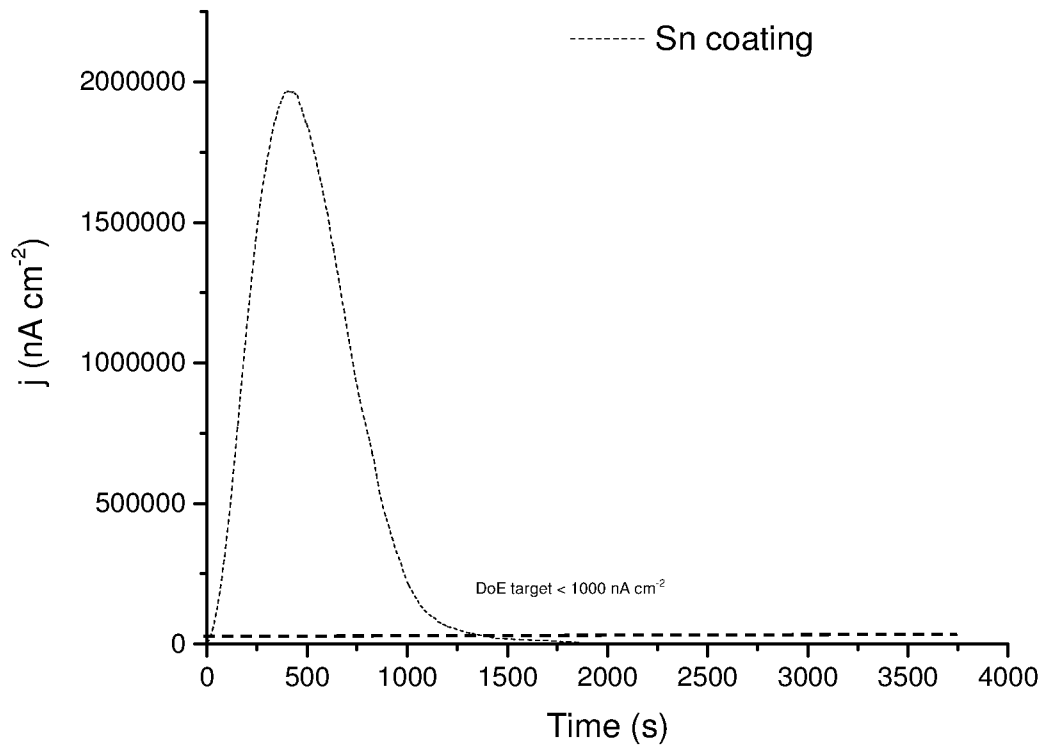


FIG. 3

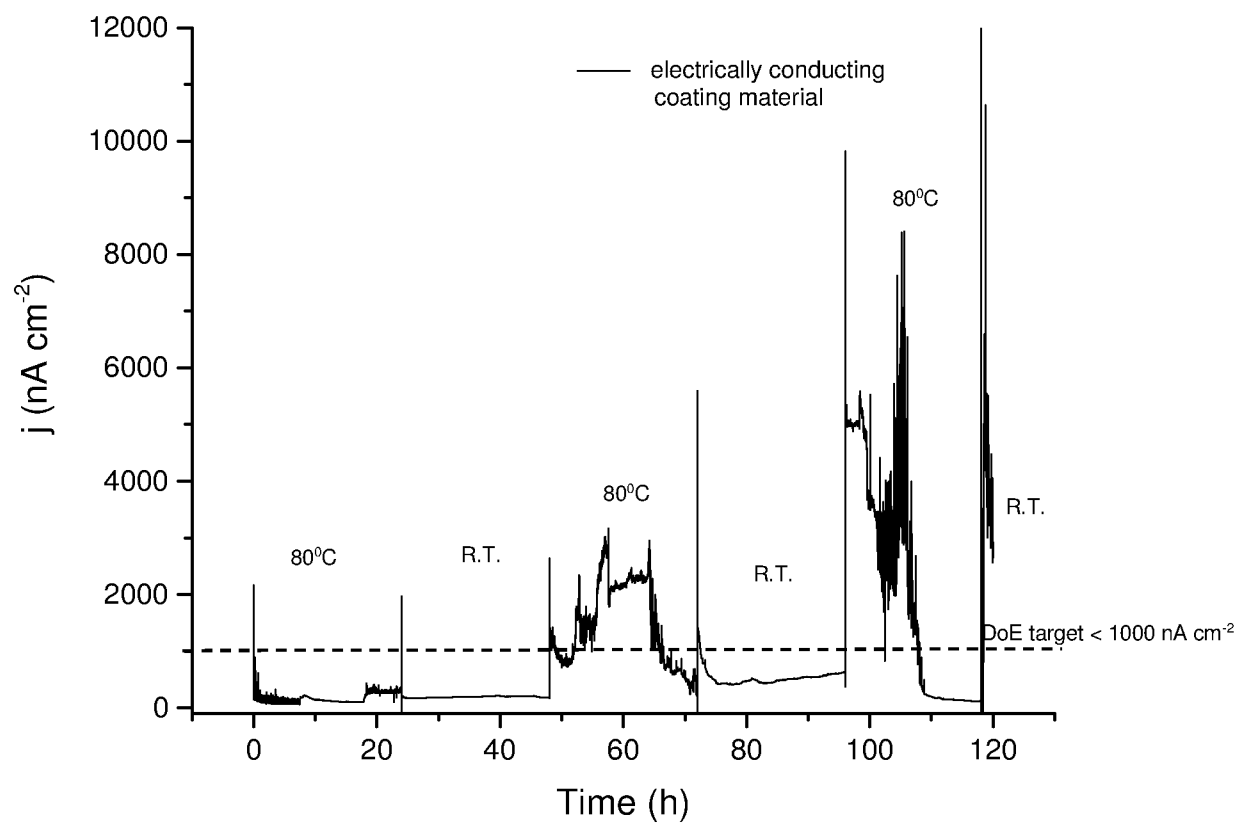


FIG.4

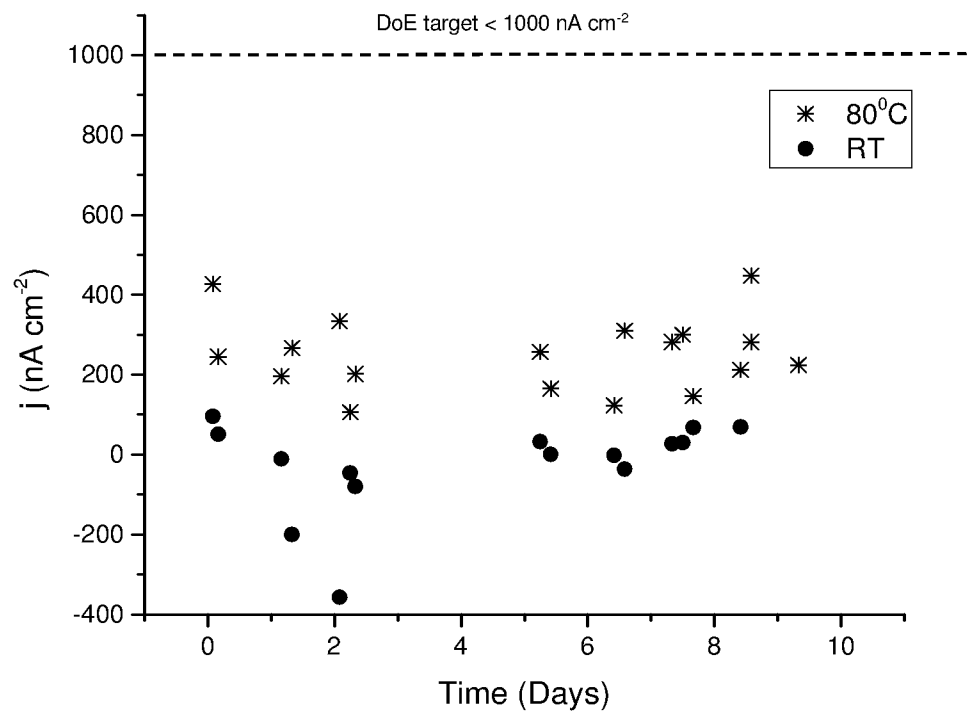
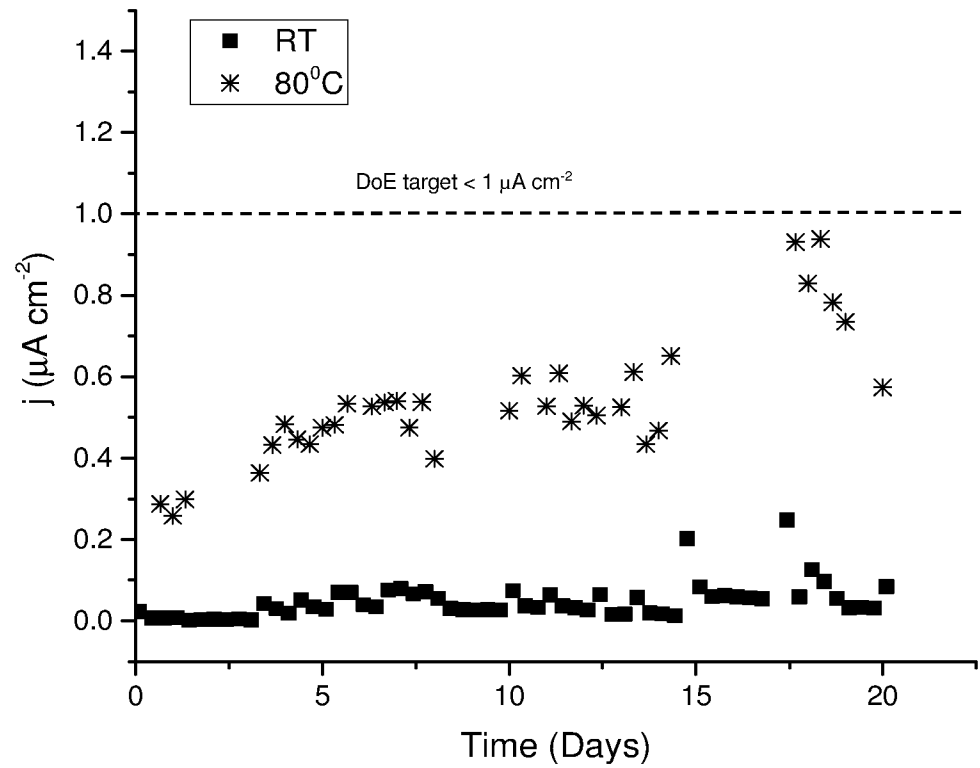


FIG.5



INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2017/051697

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01M8/0206 H01M8/0213 H01M8/0228
 ADD. H01M4/62 H01M4/66 H01M8/1018

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 C23C C23F C09D H05K

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 2009/061184 A1 (JAWOROWSKI MARK R [US] ET AL) 5 March 2009 (2009-03-05) abstract; figures 1-5 page 1, paragraph 0003 - page 3, paragraph 0035; claims 4, 18, 20, 23 -----	1-18
X	US 2010/193573 A1 (WESSLING BERNHARD [DE]) 5 August 2010 (2010-08-05) abstract; figure 1 page 1, paragraph 0002 - page 5, paragraph 0059; claim 5 -----	1,2,4-18
X	US 2005/126429 A1 (BERNARDS ROGER F [US] ET AL) 16 June 2005 (2005-06-16) page 1, paragraph 0002 - page 8, paragraph 0093; claim 13 -----	1-18



Further documents are listed in the continuation of Box C.



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Date of the actual completion of the international search

17 July 2017

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2017/051697

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009061184 A1	05-03-2009	US 2009061184 A1	05-03-2009
		US 2011287188 A1	24-11-2011

US 2010193573 A1	05-08-2010	CA 2510122 A1	23-12-2005
		DE 102004030388 A1	26-01-2006
		EP 1615484 A1	11-01-2006
		JP 4354433 B2	28-10-2009
		JP 2006044233 A	16-02-2006
		KR 20060049670 A	19-05-2006
		TW 200616789 A	01-06-2006
		US 2006019090 A1	26-01-2006
		US 2007275159 A1	29-11-2007
		US 2010193573 A1	05-08-2010

US 2005126429 A1	16-06-2005	US 2005126429 A1	16-06-2005
		US 2006102879 A1	18-05-2006
		WO 2005059057 A2	30-06-2005
