(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
01 March 2018 (01.03.2018)

WIPO | PCT

(10) International Publication Number
WO 2018/035561 A1

(51) International Patent Classification:
H01M 4/90 (2006.01) *H01M 8/02* (2016.01)

(21) International Application Number:
PCT/AU2017/050891

(22) International Filing Date:
22 August 2017 (22.08.2017)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2016903329 22 August 2016 (22.08.2016) AU

(71) Applicant: **NEWSOUTH INNOVATIONS PTY LIMITED** [AU/AU]; Rupert Myers Building, Gate 14, Barker Street, UNSW, Sydney, New South Wales 2052 (AU).

(72) Inventor: **ZHAO, Chuan**; 8/54 Avoca Street, Randwick, New South Wales 2031 (AU).

(74) Agent: **GRIFFITH HACK**; GPO Box 4164, Sydney, New South Wales 2001 (AU).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

WO 2018/035561 A1

(54) Title: FUEL CELL

(57) Abstract: The present application describes a fuel cell comprising an anode, a cathode, a non-precious metal catalyst in contact with the cathode and an electrolyte comprising a protic ionic liquid in contact with the non-precious metal catalyst.

FUEL CELL

FIELD OF THE INVENTION

The present invention relates to a fuel cell. In particular, the present invention relates to a proton exchange membrane fuel cell (PEMFC), and to a catalyst and electrolyte combination suitable for use in a proton exchange membrane fuel cell.

BACKGROUND

A fuel cell is a device that generates electricity via a chemical reaction.

A fuel cell has an anode, a cathode and an electrolyte. The reactions that produce electricity typically take place at the electrodes (i.e. at the anode and cathode). These reactions form electrons (e^-) and electrically charged particles (ions). In operation, the electrolyte facilitates the transfer of ions from one electrode to the other, whilst the electrons transfer from one electrode to the other via a connected exterior electrical circuit.

In a proton exchange membrane fuel cell, protons (H^+) and electrons (e^-) are formed at the anode, the protons transfer through the electrolyte from the anode to the cathode, while the electrons transfer to the cathode via an external electrical circuit. In a proton exchange membrane fuel cell, a membrane located between the anode and the cathode acts to permit the transfer of protons from the anode to the cathode, but impedes the transfer of electrons or anions from the anode to the cathode. Such a membrane causes electrons to flow through the external electrical circuit rather than travelling through the electrolyte.

An example of a reaction that may take place at the cathode of a PEMFC is the oxygen reduction reaction (ORR), wherein oxygen (O_2) is reduced to either H_2O_2 (from $[O_2]^{2-}$) in a 2-electron process or H_2O (from $2[O]^{2-}$) in a 4-electron process. An example of a reaction that

may take place at the anode of a PEMFC is the hydrogen oxidation reaction (HOR), wherein hydrogen (H_2) is oxidised to form protons ($2H^+$) and electrons ($2e^-$).

A catalyst is generally needed to catalyse the reactions at the cathode and the anode. The catalysts used typically comprise precious metals such as platinum. The high cost of the catalysts has limited the application of fuel cells.

As a person skilled in the art will appreciate, developments in fuel cell technology may be made in relation to any of the components of a fuel cell, either alone or in combination with the other components. For example, developments may be made in relation to the anode, the cathode, the electrolyte and/or the membrane of a fuel cell independently or in conjunction with the other components of the fuel cell.

Traditionally, developments in respect of the cathode have been slower and more challenging due to the complex nature of the reactions that typically occur at the cathode. For example, the reduction of oxygen involves many intermediates and is therefore more complex in nature than some other reduction or oxidation reactions. In addition, unfavourable energy barriers typically make the oxygen reduction reaction relatively sluggish compared to the hydrogen oxidation reaction.

It would be advantageous to provide alternative fuel cells. It would also be advantageous if at least preferred embodiments of the present invention were to provide fuel cells that do not require the use of a precious metal catalyst (such as platinum) to catalyse the reduction reaction at the cathode.

SUMMARY OF THE INVENTION

In a first aspect, the present invention provides a fuel cell comprising:

- an anode;
- a cathode;

- a non-precious metal catalyst in contact with the cathode; and

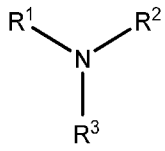
- an electrolyte comprising a protic ionic liquid in contact with the non-precious metal catalyst.

The electrolyte enables the movement of protons (or other cations) from the anode to the cathode.

Advantageously, the inventor has found that fuel cells of the present invention can be prepared in which the 4-electron reduction pathway of O_2 is favored over the 2-electron reduction pathway of O_2, thus forming H_2O rather than H_2O_2. The 4-electron reduction process is desirable from an environmental perspective as it produces water (H_2O). Further, H_2O_2 is reactive and the presence of H_2O_2 can limit the durability of fuel cells.

In an embodiment, the non-precious metal catalyst is a Fe-N/C catalyst.

In an embodiment, the protic ionic liquid has the formula $(A^-)(BH^+)$, wherein A^- is the conjugate base of acid HA, and BH^+ is the conjugate acid of base B, and the difference in pK_a between HA and BH^+ (ΔpK_a) is between about 12 and about 30. In an embodiment, the ΔpK_a is between about 15 and about 18. In an embodiment, the base B is an amine. In an embodiment, the base B is of formula (I):



(I),

wherein R^1, R^2 and R^3 are each independently selected from the group consisting of hydrogen, optionally substituted alkyl (e.g. C_{1-6}alkyl), optionally substituted alkenyl (e.g. C_{2-6}alkenyl), and optionally substituted alkynyl (e.g. C_{2-6}alkynyl);

and wherein R^1, R^2 and/or R^3 are optionally joined to form a saturated or unsaturated optionally substituted heterocycle, a saturated or unsaturated optionally substituted heterobicycle or a saturated or unsaturated optionally substituted heterotricycle.

In an embodiment, the base B is a trialkyl amine. In an embodiment, the base B is diethylmethylamine.

In an embodiment, the conjugate base A^- is the conjugate base of a strong acid. In an embodiment, the conjugate base A^- is non-nucleophilic.

In an embodiment, the conjugate base A^- is triflate (TfO^-).

In an embodiment, the protic ionic liquid is [dema][TfO].

In an embodiment, the Fe-N/C catalyst is derived from reagents including p-phenylenediamine.

In an embodiment, the Fe-N/C catalyst is derived from reagents including ferric chloride.

In an embodiment, the Fe-N/C catalyst is derived from reagents including carbon black.

In an embodiment, the Fe-N/C catalyst is derived from p-phenylenediamine, ferric chloride and carbon black.

In a second aspect, the present invention provides the use of a non-precious metal catalyst in a fuel cell to effect the $4e^-$ reduction of O_2 to H_2O in an electrolyte comprising a protic ionic liquid.

In a third aspect, the present invention provides a method of reducing O_2 to H_2O comprising contacting O_2 and a non-precious metal catalyst in an electrolyte comprising a protic ionic liquid.

In a fourth aspect, the present invention provides the reduction of O_2 to H_2O using a non-precious metal catalyst in an electrolyte comprising a protic ionic liquid.

In a fifth aspect, the present invention provides an electrode for use in a fuel cell comprising an electrolyte comprising a protic ionic liquid, the electrode having a non-precious metal catalyst on its surface.

In an embodiment of the second, third, fourth or fifth aspects, the non-precious metal catalyst is a Fe-N/C catalyst. In an embodiment, the protic ionic liquid has the formula $(A^-)(BH^+)$, wherein A^- is the

conjugate base of acid HA, and BH^+ is the conjugate acid of base B, and the difference in pK_a between HA and BH^+ (ΔpK_a) is between about 12 and about 30.

The present invention relates to developments concerning the cathode and electrolyte combination for a fuel cell. As a person skilled in the art will appreciate, conventional anodes and membranes (e.g. proton exchange membranes) may be used in the fuel cell of the present invention, provided they are compatible with the cathode and electrolyte combination.

BRIEF DESCRIPTION OF THE FIGURES

Preferred embodiments of the present invention are described below, by way of example only, with reference to the accompanying drawings in which:

Figure 1 shows (a) SEM image and (b) high magnification TEM images of fabricated Fe-N/C only catalyst. (c) deconvoluted N 1s spectrum of Fe-N/C catalyst survey scan and (d) deconvoluted Fe 2p spectrum of Fe-N/C catalyst survey scan.

Figure 2 shows (a) ring disk electrode (RDE) voltammograms of Fe-N/C in O_2 saturated [dema][TfO] at different rotation speed and at a scan rate of 0.01 V s^{-1}. (b) Corresponding Koutecky-Levich plots of Fe-N/C at various potentials. (c) rotating ring disk electrode (RRDE) voltammograms of Fe-N/C and Pt/C at 1600 rpm (ring potential is set at −0.90 V) and (d) percentage peroxide for Fe-N/C and Pt/C at various potentials (determined from the corresponding RRDE voltammograms).

Figure 3 shows chronoamperometric responses of Fe-N/C at potential −0.50 V and Pt/C at a potential of −0.15 V in (a) O_2 saturated [dema][TfO] and (b) with addition of 3 M CH_3OH.

Figure 4 shows (a) EDX line scan and (b) TEM image of fabricated Fe-N/C catalyst.

Figure 5 shows an XRD spectrum of fabricated Fe-N/C.

Figure 6 shows (a) XPS spectrum of Fe-N/C catalyst and (b) deconvoluted S 2p spectrum of Fe-N/C.

Figure 7 shows cyclic voltammograms of carbon black (CB), Fe-N/C and Pt/C loaded on glassy carbon electrodes in O_2 saturated (solid line) and Ar saturated (dash line) [dema][TfO] at the scan rate of 0.1 V s^{-1}.

Figure 8 shows (a) RDE voltammograms of Pt/C in O_2 saturated [dema][TfO] at different rotation speed (scan rate of 0.01 V s^{-1}); (b) corresponding Koutecky-Levich plots of Pt/C at various potentials.

Figure 9 shows cyclic voltammograms of Pt disk electrode in Ar-saturated [dema][TfO] (dash line) and Ar-saturated [dema][TfO] containing 50 mM H_2O_2 (solid line).

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

In a first aspect, the present invention provides a fuel cell comprising:

- an anode;
- a cathode;
- a non-precious metal catalyst in contact with the cathode; and
- an electrolyte comprising a protic ionic liquid in contact with the non-precious metal catalyst.

Electrodes

The fuel cell comprises an anode and cathode (i.e. electrodes). In use, the electrodes are electrically connected to an external electrical circuit and provide electrical power to the external circuit (i.e. do work). The electrodes may be formed of any material capable of functioning as an electrode. In the fuel cell, the electrode forms an electrical bridge or connection for electrons to move or be transported between the electrolyte and the external

electrical circuit. Accordingly, to function as an electrode, the electrode must be able to conduct electricity. Preferably, the electrode is formed of materials which are stable in, and do not react to an appreciable extent with, the electrolyte in contact with the electrode or products formed by the reactions in the fuel cell. Preferably, the electrodes have minimal resistance to maximise efficiency. Typically, the electrodes are made of a metallic or otherwise conductive substrate (such as carbon, platinum, copper, nickel etc.). In embodiments that utilise gaseous components (e.g. hydrogen and/or oxygen), the electrodes typically comprise gas diffusion layers to allow the gases to diffuse to the electrolyte (e.g. hydrogen fuel at the anode and oxygen at the cathode).

In an embodiment, the cathode comprises glassy carbon.

In an embodiment, the anode comprises platinum.

The electrodes may be formed entirely of a given material or may comprise layers of different materials. For example, an anode may be formed of platinum, or may be formed of another metal and have a platinum coating. In embodiments that have a surface coating on the electrode, the surface coating may completely coat the surface of the electrode or may coat only a portion of it. For example, an anode may be completely coated in platinum or may have only a portion of the surface coated in platinum. In some embodiments, the electrode may be formed of a largely electrically non-conductive material with a coating of an electrically conductive material.

Electrolyte

The electrolyte enables the movement of protons (or other cations) from the anode to the cathode. A single electrolyte may be in contact with both the anode and the cathode (with a proton exchange membrane in the electrolyte). However, in some embodiments, an electrolyte comprising a protic ionic liquid may be in contact with the non-precious metal catalyst in contact with the cathode, and another electrolyte may be in contact with the anode (and the catalyst on the anode), provided the combination of electrolytes enables the movement of protons (or other cations) from the anode to the cathode.

In some embodiments, the electrolyte comprising a protic ionic liquid in contact with the non-precious metal catalyst in contact with the cathode may comprise components in addition to the protic ionic liquid, such as a solvent (e.g. water). In some embodiments, the electrolyte is incorporated in a solid polymeric matrix comprising a polymeric material (e.g. sulfonated polyimides, polybenzimidazole, polyvinylidenefluoride (PVDF) etc.) to form a solid matrix comprising the electrolyte.

In an embodiment, the electrolyte comprises at least 20% v/v PIL, for example, at least about 50%, at least about 60%, at least about 70%, at least about 80%, at least about 90%, at least about 95%, at least about 97%, at least about 98%, at least about 99%, at least about 99.5%, or at least about 99.9% v/v PIL.

An ionic liquid is a salt in the liquid state. Ionic liquids typically have a melting point below about 100 °C. Protic ionic liquids are a class of ionic liquids. Protic ionic liquids are ionic liquids formed from an acid and a base, in which a proton is transferred from the acid to the base, thus forming a conjugate base and a conjugate acid.

The low vapour pressure, non-flammability, high thermal and electrochemical stability of PILs make PILs suitable for use in proton exchange membrane fuel cells (PEMFCs). These properties allow PILs to operate at higher temperatures than aqueous-based electrolytes without the need for humidification. Some commonly used proton exchange membranes, such as Nafion, rely on liquid water humidification of the membrane to transport protons. When such membranes are used with aqueous-based electrolytes, especially when operated at a temperature of about 80 to 90 °C (or above), humidification of the fuel gas is commonly used to avoid the membrane dehydrating, adding to the complexity and cost of operating such fuel cells. In some embodiments, the fuel cell of the present invention can be operated at temperatures higher than about 90 °C without humidification.

A protic ionic liquid may be described by the formula $(A^-)(BH^+)$, wherein A^- is the conjugate base of acid HA, and BH^+ is the conjugate acid of base B.

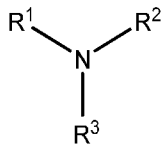
In some embodiments, the difference in pK_a between HA and BH^+ (ΔpK_a) is between about 12 and about 30, for example, between about 13 and about 25, between about 15 and about 25, between about 15 and about 20, between about 20 and about 25, between about 17 and about 20, between about 12 and about 18, between about 16 and about 19, between about 17 and about 19.

In an embodiment, the base B is an amine.

In an embodiment, the base B is a tertiary amine.

In an embodiment, the base B is a trialkyl amine, for example, triethylamine, dimethylethylamine, diethylmethylamine.

In an embodiment, the base B is of formula (I):



(I),

wherein R^1, R^2 and R^3 are each independently selected from hydrogen, optionally substituted alkyl (e.g. C_{1-6}alkyl), optionally substituted alkenyl (e.g. C_{2-6}alkenyl), and optionally substituted alkynyl (e.g. C_{2-6}alkynyl);

and wherein R^1, R^2 and/or R^3 are optionally joined to form a saturated or unsaturated optionally substituted heterocycle, a saturated or unsaturated optionally substituted heterobicycle or a saturated or unsaturated optionally substituted heterotricycle.

In some embodiments, the base B is an imine. For example, the base B may include 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

In some embodiments, the conjugate base A^- is the conjugate base of a strong acid. Strong acids typically have a pK_a of less than 0, for example, between about 0 and about -20, between about 0 and about -15, between about 0 and about -10, between about 0 and about -5, between about -1 and about -15, between about -1 and about -10,

between about -1 and about -5, between about -2 and about -15, between about -2 and about -10, between about -2 and about -5, between about -3 and about -10, between about -4 and about -10, between about -5 and about -10, between about -6 and about -8, between about -10 and about -20, between about -10 and about -15, between about -5 and about -15 or between about -12 and about -16.

The pK_a values of common acids (and conjugate acids of common bases) are widely reported in the literature and are well measured. For example, Evans' pK_a table (http://evans.rc.fas.harvard.edu/pdf/evans_pKa_table.pdf) and the Bordwell pK_a table (http://www.chem.wisc.edu/areas/reich/pkatable/index.htm) provide the pK_a values of many common acids (and conjugate acids of common bases).

Examples of strong acids which may be useful for forming the protic ionic liquid for use in a fuel cell of the present invention include triflic acid (CF_3SO_3H, TfOH) and other fluorinated alkyl sulfonic acids (e.g. $F_9C_4SO_3H$), methanesulfonic acid (CH_3SO_3H, MsOH), trifluoroacetic acid (CF_3CO_2H, TFA) and trifluoromethanesulfonimide ($(CF_3SO_2)_2NH$, also known as bistriflimide or bis(trifluoromethane)sulfonimide).

Mixtures of two or more acids and/or two or more bases may be used to form the PIL. For example, a PIL may comprise more than one conjugate base (e.g. two or more of TfO^-, $F_9C_4SO_3^-$, $CF_3CO_2^-$, $CH_3SO_3^-$ or $(CF_3SO_2)_2N^-$), and/or more than one conjugate acid (e.g. two or more of triethylammonium, dimethylethylammonium or diethylmethylammonium). Such mixtures may be prepared by mixing two different PILs, or may be made by adding two or more acids with a base, two or more bases with an acid, or two or more acids with two or more bases.

Suitable acid HA and base B pairs may be selected based on their reported or predicted ΔpK_a value. In such embodiments, the ΔpK_a may be chosen to optimise the open circuit potential (OCP) of the protic ionic liquid derived from the acid HA and base B pair. It has been reported that the OCP may depend on the ΔpK_a value of the protic

ionic liquid. For example, a protic ionic liquid having ΔpK_a value in the range of about 12 to about 16 or about 19 to about 21 would be expected to have an OCP in the range of about 0.7 to about 0.9 V. In contrast, a protic ionic liquid having ΔpK_a value in the range of about 16 to about 19 would be expected to have an OCP in the range of about 0.9 to about 1.1 V. Accordingly, in some embodiments, the protic ionic liquid has an OCP in the range of about 0.7 to about 1.1 V, for example, between about 0.9 to about 1.1, 1.0 to about 1.1 V.

In some embodiments, the conjugate base A^- is non-nucleophilic. A non-nucleophilic conjugate base is a conjugate base that is substantially non-nucleophilic (i.e. a poor nucleophile or compound that does not act as a nucleophile to an appreciable extent). Without wishing to be bound by theory, it is believed that a non-nucleophilic conjugate base A^- is less likely to bind to a nucleophilic site of the non-precious metal catalyst (which may also be an active site of the catalyst). An example of a non-nucleophilic conjugate base is triflate (TfO^-), which is usually obtained from triflic acid (TfOH). Other non-nucleophilic conjugate bases include sterically encumbered conjugate bases.

In an embodiment, the protic ionic liquid is diethylmethylammonium trifluoromethanesulfonate [dema][TfO]. Diethylmethylammonium trifluoromethanesulfonate [dema][TfO] exhibits a high and stable open circuit potential (OCP) (1.03 V) at 150 °C which is better than anhydrous phosphoric acid under same conditions. The better electrochemical performance of [dema][TfO] may be attributed to its intermediate N-H bond strength and ΔpKa. Diethylmethylammonium bis(trifluoromethylsulfonyl)imide, [dema][NTf_2], which has similar bulk properties as [dema][TfO], exhibits lower OCP (0.70 V) than [dema][TfO] under same conditions, likely due to the relatively slower kinetics of ORR and HOR. The poor electrochemical activity for ORR and HOR of [dema][NTf_2] is likely due to lower proton activity resulting from a theoretically stronger N-H bond. Due to the enhanced kinetics of ORR and HOR, [dema][TfO] is a suitable electrolyte for non-humidified fuel cells.

The protic ionic liquid is in a liquid state when the fuel cell of the present invention is in use. As a person skilled in the art will appreciate, a fuel cell may be operated at various temperatures and protic ionic liquids may solidify at lower temperatures. The protic ionic liquid is a liquid at the operating temperature of the fuel cell. Typically, the protic ionic liquid has a melting point below about 100 °C (e.g. below about 80 °C, below about 50 °C or below about 20 °C).

Membrane

A proton exchange membrane fuel cell comprises a membrane disposed between the anode and the cathode. The membrane acts to permit protons (or other cations) to pass or conduct through the membrane while inhibiting or impeding the passage or conduction of electrons. This acts to inhibit or impede the direct passage of electrons through the electrolyte between the anode and cathode; instead they must pass through an external electrical circuit. The membrane typically also prevents the fuel and oxygen from passing through, maintaining the separation of the fuel and oxygen in the fuel cell. Alternatively, an additional membrane may be used for this purpose.

The membrane may, for example, be formed of a proton conducting polymer, such as Nafion (a sulfonated tetrafluoroethylene based fluoropolymer-copolymer).

A variety of proton exchange membranes are commercially available and may be used in the fuel cell of the present invention. Such membranes include Nafion membranes produced by DuPont (e.g. Nafion HP, Nafion 211, Nafion XL, Nafion 212, Nafion NE1035, Nafion 115, Nafion 117, Nafion 1110, Nafion N2100TX, Aciplex (produced by Asahi Chemical Company), Flemion (produced by Asahi Chemical Company), BAM (produced by Ballard Advanced Materials Corporation), and SEBS (Dais Analytic Corporation). In addition, membranes comprising polyvinylidenefluoride (PVDF) and its derivatives may also be used.

Non-precious metal catalyst

The fuel cell of the present invention comprises a non-precious metal catalyst in contact with the cathode.

As used herein, the term "precious metal catalyst" refers to a catalyst comprising a precious metal (Pt, Pd, Ag or Rh), and the term "non-precious metal catalyst" refers to a catalyst that does not comprise a precious metal (Pt, Pd, Ag or Rh) or does not comprise a precious metal (Pt, Pd, Ag or Rh) in any appreciable amount. The "non-precious metal catalyst" in contact with the cathode typically comprises less than 0.05 mg/cm^2 of a precious metal (Pt, Pd, Ag or Rh).

The inventors have found that fuel cells can be prepared comprising a protic ionic liquid electrolyte and a non-precious metal catalyst in contact with the cathode. A limiting factor for many potential applications of fuel cells is the cost of the precious metal catalysts commonly used in fuel cells, and therefore it is advantageous to provide a fuel cell in which at least the catalyst in contact with the cathode is a non-precious metal catalyst.

The non-precious metal catalyst is capable of catalysing the reduction of O_2 in the electrolyte comprising the protic ionic liquid. Preferably the catalyst is capable of catalysing the $4e^-$ reduction of oxygen to water in the electrolyte comprising the protic ionic liquid.

The inventor has found that by combining a non-precious metal catalyst on the cathode with an electrolyte comprising a PIL in contact with the non-precious metal catalyst, it is possible to prepare a fuel cell comprising a non-precious metal catalyst in contact with the cathode, in which the non-precious metal catalyst is capable of catalyzing the $4e^-$ reduction of oxygen to water.

To the best of the inventor's knowledge, the 4-electron reduction of O_2 in a protic ionic liquid has previously only been achieved using platinum catalysts. The inventor has now surprisingly found that a non-precious metal catalyst can be used to catalyse the oxygen reduction reaction in a PIL. The inventor has also surprisingly found that the combination of a non-precious metal catalyst and a PIL may be used to effect the $4e^-$ reduction of O_2 to H_2O (via $2[O]^{2-}$) at a low overpotential.

The non-precious metal catalyst is present in the fuel cell to catalyse the reduction of oxygen. In an embodiment, the non-precious metal catalyst catalyses the reduction of oxygen from O_2 to $[O_2]^{2-}$ (which may form H_2O_2 upon addition of $2H^+$). In another embodiment, the non-precious metal catalyst catalyses the reduction of $[O_2]^{2-}$ (or H_2O_2) to $2[O]^{2-}$ (thus forming H_2O upon addition of $2H^+$). In another embodiment, the the non-precious metal catalyst catalyses the reduction of oxygen from O_2 to $2[O]^{2-}$ (thus forming $2H_2O$ upon addition of $4H^+$).

In some embodiments, the non-precious metal catalyst is on the entire surface (e.g. covers the entire surface) of the cathode. In other embodiments, the non-precious metal catalyst is on just a portion (e.g. covers only a portion) of the surface of the cathode.

The catalyst may be brought into contact with the electrode by any means that results in the catalyst being in contact with the electrode. The catalyst may be formed on the surface of the electrode. More typically, the catalyst is pre-formed and then applied to the surface of the electrode. A composition comprising the catalyst in a solvent and/or a binder may be used to assist with forming a layer of the catalyst on the electrode.

The non-precious metal catalyst in contact with the cathode may be a Fe-N/C catalyst.

Accordingly, in an aspect, the present invention provides a fuel cell comprising:

- an anode;
- a cathode;
- a Fe-N/C catalyst in contact with the cathode; and
- an electrolyte comprising a protic ionic liquid in contact with the Fe-N/C catalyst.

Fe-N/C catalysts may be made using various known methods. Fe-N/C catalysts can also be made using a variety of different conditions and starting materials, which can give rise to Fe-N/C catalysts with

differing properties (e.g. different tolerances to different PILs, temperature, catalytic turnover etc.).

Starting materials for making Fe-N/C catalysts typically include an iron source, a nitrogen source and a carbon source. For example, iron sources that may be used for making Fe-N/C catalysts include iron (II) or iron (III) salts such as $FeCl_3$, $Fe(NO_3)_3$, $Fe(acetylacetate)_3$ and $FeSO_4$. Nitrogen sources that may be used for making Fe-N/C catalysts include p-phenylenediamine, m-phenylenediamine, o-phenylenediamine, aniline and 2,4,6-tris(2-pyridyl)-s-triazine. Carbon sources that may be used for making Fe-N/C catalysts include amorphous carbon (e.g. carbon black). Other carbon sources may also be used.

The Fe-N/C catalyst is typically prepared by pyrolysing the starting materials. The temperature at which the pyrolysis reaction takes place can vary significantly depending on the starting materials that are to be employed in making the Fe-N/C catalyst. A person skilled in the art will be able to determine a suitable temperature at which to perform the pyrolysis reaction. The pyrolysis reaction typically takes place at above about 200 °C, for example, between about 200 and about 2000 °C, between about 200 and about 1500 °C, between about 300 and about 1000 °C, between about 500 and about 1000 °C or between about 800 and about 1000 °C.

In some embodiments, the Fe-N/C catalyst is prepared by pyrolysing:

- an iron source selected from $FeCl_3$, $Fe(NO_3)_3$, $Fe(acetylacetate)_3$ and $FeSO_4$ or a combination thereof;

- a nitrogen source selected from p-phenylenediamine, m-phenylenediamine, o-phenylenediamine, aniline and 2,4,6-tris(2-pyridyl)-s-triazine or a combination thereof; and

- amorphous carbon.

In an embodiment, the Fe-N/C catalyst is derived from p-phenylenediamine, ferric chloride and carbon black. In an embodiment, the Fe-N/C catalyst is prepared by pyrolysing p-phenylenediamine, ferric chloride and carbon black.

In some embodiments, the Fe-N/C catalyst has nanostructured Fe-N/C particles which are relatively uniform and well dispersed. In some embodiments, the Fe-N/C catalyst has a high proportion of pyridinic N and graphitic N sites compared to Fe_3C and FeS sites. A person skilled in the art will be able to determine the proportion of such sites using known techniques. For example, the pyridinic N and graphitic N sites in an Fe-N/C catalyst may be identified and quantified using a combination of different techniques (e.g. XRD, scanning transmission electron microscopy (STEM), high resolution transmission electron microscopy (HRTEM) and XPS). FeS and Fe3C can be detected by using XRD and STEM/HRTEM. Peak intensities and peak positions in the XPS spectrum respectively provide information about the quantity of sites as well as elemental/chemical composition.

Compared to some Pt/C catalysts, the Fe-N/C catalyst may be easily produced and/or produced at lower cost, thus making it attractive for large scale commercial applications.

Fuel cell

In operation, the fuel (e.g. H_2 gas) is brought into contact with the anode, whilst oxygen (e.g. from air) is brought into contact with the cathode (e.g. by dissolution in the electrolyte).

At the anode, a chemical reaction oxidises the fuel to form protons and electrons. Typically a catalyst is in contact with the anode to catalyse this reaction. The catalyst in contact with the anode may be any catalyst capable of catalysing the reaction and may be a precious metal catalyst (e.g. a Pt catalyst) or a non-precious metal catalyst. The electrolyte in contact with the anode enables the movement of protons from the anode to the cathode.

At the cathode, the oxygen combines with the electrons that have travelled or been conducted though the external electrical circuit and the protons that have travelled or been conducted through the electrolyte from the anode thereby reducing oxygen to either H_2O_2 or H_2O, preferably H_2O. The non-precious metal catalyst (e.g. the Fe-N/C catalyst) catalyses this reaction (the reduction of the oxygen). Preferably, the oxygen is reduced to H_2O as water is a relatively inert and environmentally safe product. Furthermore, the

presence of H_2O_2 within the fuel cell can reduce the durability of the fuel cell.

Typically multiple fuel cells are combined in series (a fuel cell stack) to increase the voltage generated. Fuel cells may also be combined in parallel to increase the current delivery (i.e. increase the overall current output (Amps)).

Definitions

Unless otherwise herein defined, the following terms will be understood to have the general meanings which follow. The terms referred to below have the general meanings which follow when the term is used alone and when the term is used in combination with other terms, unless otherwise indicated. Hence, for example, the definition of "alkyl" applies to "alkyl" as well as the "alkyl" portions of "arylC_{1-6}alkyl", "heteroarylC_{1-6}alkyl" etc.

The term "alkyl" refers to a straight chain or branched chain saturated hydrocarbyl group. Preferred are C_{1-6}alkyl and C_{1-4}alkyl groups. The term "C_{1-6}alkyl" refers to an alkyl group having 1 to 6 carbon atoms. Examples of C_{1-6}alkyl include methyl (Me), ethyl (Et), propyl (Pr), isopropyl (i-Pr), butyl (Bu), isobutyl (i-Bu), sec-butyl (s-Bu), tert-butyl (t-Bu), pentyl, neopentyl, hexyl and the like. Unless the context requires otherwise, the term "alkyl" also encompasses alkyl groups containing one less hydrogen atom such that the group is attached via two positions, i.e. divalent.

The term "alkenyl" refers to a straight chain or branched chain hydrocarbyl group having at least one double bond of either *E*- or *Z*- stereochemistry where applicable. Preferred are C_{2-6}alkenyl and C_{2-4}alkenyl groups. The term "C_{2-6}alkenyl" refers to an alkenyl group having 2 to 6 carbon atoms. Examples of C_{2-6}alkenyl include vinyl, 1-propenyl, 1- and 2-butenyl and 2-methyl-2-propenyl. Unless the context requires otherwise, the term "alkenyl" also encompasses alkenyl groups containing one less hydrogen atom such that the group is attached via two positions, i.e. divalent.

The term "alkynyl" refers to a straight chain or branched chain hydrocarbyl group having at least one triple bond. Preferred are

C_{2-6}alkynyl and C_{2-4}alkynyl groups. The term "C_{2-6}alkynyl" refers to an alkynyl group having 2 to 6 carbon atoms. Examples of C_{2-6}alkynyl include ethynyl, 1-propynyl, 1- and 2-butynyl, 2-pentynyl, 3-pentynyl, 4-pentynyl, 2-hexynyl, 3-hexynyl, 4-hexynyl and 5-hexynyl and the like. Unless the context indicates otherwise, the term "alkynyl" also encompasses alkynyl groups containing one less hydrogen atom such that the group is attached via two positions, i.e. divalent.

The terms "hydroxy" and "hydroxyl" refer to the group -OH.

The term "alkoxy" refers to an alkyl group as defined above covalently bound via an O linkage, such as methoxy, ethoxy, propoxy, isoproxy, butoxy, tert-butoxy and pentoxy. Preferred are C_{1-6}alkoxy, C_{1-4}alkoxy and C_{1-3}alkoxy groups.

The term "carboxylate" or "carboxyl" refers to the group $-COO^-$ or -COOH.

The term "ester" refers to a carboxyl group having the hydrogen replaced with, for example, an alkyl group ("alkylester" or "alkylcarbonyl"), an aryl or aralkyl group ("arylester" or "aralkylester") and so on. CO_2C_{1-3}alkyl groups are preferred, such as for example, methylester ($-CO_2Me$), ethylester ($-CO_2Et$) and propylester ($-CO_2Pr$) and reverse esters thereof (e.g. -OC(O)Me, -OC(O)Et and -OC(O)Pr).

The term "amino" refers to the group $-NH_2$.

The term "substituted amino" or "secondary amino" refers to an amino group having a hydrogen replaced with, for example, an alkyl group ("alkylamino"), an aryl or aralkyl group ("arylamino", "aralkylamino") and so on. C_{1-3}alkylamino groups are preferred, such as for example, methylamino (-NHMe), ethylamino (-NHEt) and propylamino (-NHPr).

The term "disubstituted amino" or "tertiary amino" refers to an amino group having the two hydrogens replaced with, for example, an alkyl group, which may be the same or different ("di(alkyl)amino"), an aryl and alkyl group ("aryl(alkyl)amino") and so on. Di(C_{1-3}alkyl)amino groups are preferred, such as, for example,

dimethylamino (-NMe_2), diethylamino (-NEt_2), dipropylamino (-NPr_2) and variations thereof (e.g. -N(Me)(Et) and so on).

The term "acyl" or "aldehyde" refers to the group -C(=O)H.

The term "substituted acyl" or "ketone" refers to an acyl group having the hydrogen replaced with, for example, an alkyl group ("alkylacyl" or "alkylketone"), an aryl group ("arylketone"), an aralkyl group ("aralkylketone") and so on. C_{1-3}alkylacyl groups are preferred.

The term "amido" or "amide" refers to the group -C(O)NH_2.

The term "aminoacyl" refers to the group -NHC(O)H.

The term "substituted amido" or "substituted amide" refers to an amido group having a hydrogen replaced with, for example, an alkyl group ("alkylamido" or "alkylamide"), an aryl ("arylamido"), aralkyl group ("aralkylamido") and so on. C_{1-3}alkylamide groups are preferred, such as, for example, methylamide (-C(O)NHMe), ethylamide (-C(O)NHEt) and propylamide (-C(O)NHPr) and reverse amides thereof (e.g. -NHC(O)Me, -NHC(O)Et and -NHC(O)Pr).

The term "disubstituted amido" or "disubstituted amide" refers to an amido group having the two hydrogens replaced with, for example, an alkyl group ("di(alkyl)amido" or "di(alkyl)amide"), an aralkyl and alkyl group ("alkyl(aralkyl)amido") and so on. Di(C_{1-3}alkyl)amide groups are preferred, such as, for example, dimethylamide (-C(O)NMe_2), diethylamide (-C(O)NEt_2) and dipropylamide (-C(O)NPr_2) and variations thereof (e.g. -C(O)N(Me)Et and so on) and reverse amides thereof.

Unless otherwise defined, the term "optionally substituted" as used herein indicates a group may or may not be substituted with 1, 2, 3, 4 or more groups, preferably 1, 2 or 3 groups, more preferably 1 or 2 groups, independently selected from the group consisting of alkyl (e.g. C_{1-6}alkyl), alkenyl (e.g. C_{2-6}alkenyl), alkynyl (e.g. C_{2-6}alkynyl), cycloalkyl (e.g. C_{3-8}cycloalkyl), hydroxyl, oxo, alkoxy (e.g. C_{1-6}alkoxy), aryloxy, arylC_{1-6}alkoxy, halo, haloC_{1-6}alkyl (such as -CF_3 and -CHF_2), haloC_{1-6}alkoxy (such as -OCF_3 and -$OCHF_2$), carboxyl, esters, cyano, nitro, amino, substituted amino,

disubstituted amino, acyl, ketones, amides, aminoacyl, substituted amides, disubstituted amides, aryl, arylC_{1-6}alkyl, heterocyclylC_{1-6}alkyl, arylC_{2-6}alkenyl, heterocyclylC_{2-6}alkenyl, arylC_{2-6}alkynyl, heterocyclylC_{2-6}alkynyl, heteroarylC_{1-6}alkyl, heteroarylC_{2-6}alkenyl, heteroarylC_{2-6}alkynyl, heterocyclyl and heteroaryl, wherein each alkyl, alkenyl, alkynyl, cycloalkyl, aryl and heterocyclyl and groups containing them may be further optionally substituted. Optional substituents in the case of heterocycles containing N may also include but are not limited to C_{1-6}alkyl i.e. N-C_{1-6}alkyl.

For optionally substituted "alkyl", "alkenyl" and "alkynyl", the optional substituent or substituents are preferably selected from amino, substituted amino, disubstituted amino, aryl, halo (e.g. F, Cl, Br, I), heterocyclyl, C_{1-6}alkoxy, hydroxyl, oxo, aryloxy, carboxyl, carboxylate and esters. Each of these optional substituents may also be optionally substituted with any of the optional substituents referred to above.

EXAMPLES

The present invention is further described below by reference to the following non-limiting Examples.

Example 1

1 Methods

1.1 Materials and methods

Diethylmethylamine (97%), trifluoromethanesulfonic acid (TfOH) (98%), *p*-phenylenediamine (*p*-PD) (≥ 99%), Nafion solution (5 wt%), potassium chloride (KCl) (≥ 99%) and Pt/C (10 wt% Pt) were purchased from Sigma Aldrich. Conductive carbon black (Super C-65) was purchased from Timcal. Potassium ferricyanide ($K_3[Fe(CN)_6]$), ammonium peroxydisulfate (APS) (98%), and hydrogen peroxide (H_2O_2) (30%) were purchased from Chem Supply. Ferric chloride ($FeCl_3$) (97%) was purchased from Strem Chemicals and hydrochloric acid (HCl) (32%) was purchased from RCI Labscan. Oxygen (high purity) and argon (high purity) were purchased from Air Liquide.

2 Synthesis and Characterisation

2.1 Synthesis of PIL

The PIL, [dema][TfO], was synthesized and characterized using the procedure described previously (A. Khan, X. Lu, L. Aldous, C. Zhao, *J. Phys. Chem. C* 2013, *117*, 18334-18342; X. Lu, G. Burrell, F. Separovic, C. Zhao, *J. Phys. Chem. B* **2012**, *116*, 9160-9170; C. Zhao, G. Burrell, A. A. J. Torriero, F. Separovic, N. F. Dunlop, D. R. MacFarlane, A. M. Bond, *J. Phys. Chem. B* **2008**, *112*, 6923-6936).

Briefly, equimolar amounts (1:1 mol/mol) of Brønsted acid and base were added dropwise simultaneously while stirring vigorously to dissipate the heat of the exothermic reaction. Prior to each experiment, [dema][TfO] was further dried at 80 °C under vacuum for 48 hours. After drying, Karl Fischer titrations were performed using a Metrohm 831 KF coulometer (Herisau, Switzerland) to confirm the water content in the PILs were below 200 ppm. The viscosity and density of [dema][TfO] were recorded using Anton Paar Lovis 2000 ME

Microviscometer (MEP Instruments Pty Ltd, Australia) at a temperature of 25 °C.

2.2 Synthesis of Fe-N/C Catalyst

The Fe-N/C based catalyst was synthesized by pyrolysing polymerised *p*-phenylenediamine, ferric chloride and carbon black (Y. Zhu, B. Zhang, X. Liu, D.-W. Wang, D. S. Su, *Angew. Chem. Int. Ed.* **2014**, *53*, 10673-10677).

Briefly, acid treated carbon black was dispersed in p-phenylenediamine in 0.5 M HCl followed by slow addition of aqueous solution of ammonium peroxydisulfate while keeping the temperature below 10°C. An aqueous solution of $FeCl_3$ (1:4 molar ratio of $FeCl_3$ to phenylenediamine) was slowly added to the suspension. The mixture was continuously stirred for 24 hours after which the solvent was removed using a rotary evaporator. The precursor was heat-treated at 900°C under argon atmosphere for 1 hour, pre-leached with 1 M HCl at 80°C for 8 hours to remove unstable and inactive species and thoroughly rinsed with ultra-pure water. Finally, the catalyst was again heat-treated at 900°C under argon atmosphere for 3 hours to obtain the Fe-N/C catalyst.

2.3 Physical characterization

Scanning electron microscope (SEM) images of Fe-N/C were recorded using FEI Nova NanoSEM 230 with a Bruker Energy Dispersive X-Ray (EDX) system operated on 10 kV accelerating voltage. Transmission electron microscopy (TEM) was performed on a Philips CM 200 at 200 kV. The sample was prepared by drop casting ethanol suspensions onto copper grids. The XRD samples were prepared by drop casting the ethanol suspension onto the glass substrates while XPS measurements were carried out on a Thermo ESCALAB250i X-ray Photoelectron Spectrometer employing a monochromatic Al K α x-ray source (energy 1,486.68 eV).

2.3.1 Electrochemical characterisation

All the electrochemical measurements were performed on a CHI 760D bipotentiostat (CH Instruments) in a custom built electrochemical cell. For all electrochemical experiments, a rotating ring disk

electrode (RRDE) with a glassy carbon (GC) disk (0.125 cm^2) and Pt ring (0.188 cm^2) (ALS Co., Ltd, Japan) was employed as working electrode. A constant flow of either oxygen or argon was maintained over the solution through a gas bubbler providing constant overpressure to prevent atmospheric contamination. The collection efficiency of the RRDE electrode was 41 % (estimated using 5 mM $K_3[Fe(CN)_6]$ in 1.0 M KCl solution). Pt wire and Ag wire were employed as counter and quasi reference electrodes, respectively. The Ag QRE was found to be relatively stable.

2.3.2 Loading of the catalysts

A Fe-N/C catalyst "ink" was prepared by dispersing 9 mg of catalyst in isopropanol/water (0.2 mL, 3:1 v/v) followed by addition of Nafion (20 µL). The suspension was then sonicated for 30 minutes to get a homogenous "ink" of the catalyst. 5 µL of "ink" was drop casted to the GC disk and left to dry in air resulting in a catalyst loading of 1.8 mg cm^{-2}. In case of Pt/C and carbon black (after treatment with 6 M HCl for 24 hours to remove any impurities), the catalyst loading was 1.0 mg cm^{-2}. All rotating disk electrode (RDE) and RRDE voltammograms were 95% ohmic drop (iR drop) compensated using same potentiostat while cyclic voltammetric and amperometric measurements were recorded without any *iR* compensation. For RDE measurements, the disk electrode was scanned cathodically at a scan rate of 10 mV s^{-1} at varying rotation rate from 100-1600 rpm. The number of electrons (n) was calculated from the slopes of the linear fits of Koutecky-Levich plots according to the Koutecky-Levich equation:

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_K} \qquad (1)$$

$$j_L = 0.62nFD^{2/3}\omega^{1/2}\nu^{1/6}c \qquad (2)$$

where j is the measured current density, j_L and j_K are diffusion limiting and kinetics current densities, n is the number of electrons transferred, ω is the angular velocity of the disk ($\omega = 2\pi f$, f is the linear rotation speed), F is Faraday constant (96,485 C mol^{-1}), ν is the kinematic viscosity of [dema][TfO] (0.225 cm^2 s^{-1}),

D is the diffusion coefficient of O_2 in [dema][TfO] ($1.1 \pm 0.2 \times 10^{-5}$ cm^2 s^{-1}), c is the concentration of O_2 in [dema][TfO] ($1.79 \pm 0.04 \times 10^{-3}$ mol/L).

From the RRDE measurements, the number of electrons transferred and the percentage yield of H_2O_2 produced at the disk electrode during the ORR are calculated according to the following equations:

$$\%H_2O_2 = 200 \times \frac{\left[\frac{i_R}{N}\right]}{i_D + \left[\frac{i_R}{N}\right]} \quad (3)$$

$$n = 4 \times \frac{i_D}{i_D + \left[\frac{i_R}{N}\right]} \quad (4)$$

where i_D is disk current, i_R is ring current and N is the current collection efficiency of the Pt ring (0.41 determined from the reduction of $K_3[Fe(CN)_6]$.

Example 2

In this example, a Fe-N/C based catalyst was prepared and its catalytic activity in the oxygen reduction reaction (ORR) in a PIL ([dema][TfO]) was investigated and compared with a commercially available Pt/C catalyst.

To the best of the inventor's knowledge, this work represents the first non-precious metal based catalyst capable of catalysing the $4e^-$ reduction of oxygen to water in a protic ionic liquid.

The inventor surprisingly found that Fe-N/C can catalyse the $4e^-$ reduction of oxygen to water in [dema][TfO] with high catalytic activity - approaching that of Pt/C, and displayed a durability that was higher than Pt-based catalysts. These results demonstrate that such a system may be capable of reducing the cost associated with Pt-based catalysts and humidification of aqueous electrolytes, and may thus assist in the future large scale implementation of fuel cells based on this technology.

The PIL, [dema][TfO], was synthesized and characterized using the procedure described in Example 1. The Fe-N/C catalyst was prepared by pyrolysing p-phenylnediamine, ferric chloride and carbon black as described in Example 1. The SEM image (Figure 1a) shows the nanostructured Fe-N/C particles which are relatively uniform and well dispersed. The presence of Fe and N in the resulted carbon is detected by an EDX line scan detection mode, Figure 4a. From the TEM image (Figure 4b), the Fe-N/C sample showed amorphous-like carbon particles of size 50 ~ 80 nm. High magnification TEM (Figure 1b) reveals that graphite lattice is not well developed while no crystalline metal or metal sulphide phases are observed. XRD is applied to further characterise the crystalline structure and phase composition of Fe-N/C catalyst. The XRD pattern of the Fe-N/C catalyst confirmed the non-crystallinity (or at least minimal crystallinity) of the material with only a broader peak at 18-30 2θ, Figure 5. No diffraction peaks for Fe3C and FeS were observed, supporting the observations made by TEM images.

In developing the present system, it was useful to determine the nature of the active sites of the Fe-N/C catalyst for improving the ORR electrocatalytic activity of the catalyst. In this regard, Fe_3C and FeS sites are not known to be active sites for the ORR and are possibly removed during the acid leaching process (due to their poor stability in acid). In forming the Fe-N/C catalyst, pyrolysis at high temperature induces decomposition of polymerised *p*-phenylenediamine in the precursors containing P-*p*PD- or P-*m*PD-coated carbon and $FeCl_3$ that leads to rearrangement of Fe, nitrogen and carbon to form FeN complexes bonded into carbon support. It is expected that the electrochemical activity of Fe-N/C is due to presence of Fe-N complexes in the catalyst.

More information concerning the chemical state of doped Fe-N/C catalyst was acquired by XPS. The XPS survey scan, Figure 6a, shows the bonding configurations of carbon, nitrogen, oxygen, iron and sulphur for the catalyst. The N 1s spectrum, Figure 1c, can be deconvoluted into two peaks at 398.5 and 401.09 eV, which can be assigned to pyridinic N and graphitic N, respectively, corresponding to their respective binding energies. It has been previously

reported that both the graphitic N and pyridinic N play a crucial role in the catalytic activity of oxygen reduction. The Fe 2p spectrum (Figure 1d) can be deconvoluted into four peaks. The peaks with binding energies of 710.0 and 715.0 eV are attributed to the $2p_{3/2}$ orbitals of Fe^{2+} and Fe^{3+} species, respectively, while the peaks at 723.0 and 728.0 eV can be assigned to the binding energies of $2p_{1/2}$ orbitals of Fe^{2+} and Fe^{3+} species, respectively. The pyridinic-N atoms have been reported to serve as metal coordination sites due to the lone pair of electrons and the presence of pyridinic-N atoms in the catalyst suggests that Fe may be present in the Fe-N/C catalyst in the form of Fe-N complexes.

From the detailed S 2p spectrum (Figure 6b), only peaks associated with S-C species (163.7 and 164.8 eV) and SOx species (167.9 and 168.8 eV) are observed. No peak associated with the FeS is detected, indicating that any FeS generated was washed out during the acid leaching process, which is in agreement with the XRD and TEM analysis.

Figure 7 shows the CVs obtained at CB, Fe-N/C and Pt/C in O_2 saturated [dema][TfO], respectively. In the case of Fe-N/C, a reversible redox process, attributed to Fe^{3+}/Fe^{2+} process, is observed at a formal potential of 0.33 V, similar to that previously reported for pyrolysed Fe-N/C catalyst in 0.5 M H_2SO_4 solution. The ORR was found to overlap significantly with the Fe^{3+}/Fe^{2+} process, and shows a much more positive ORR onset potential (~ 0.235 V vs Ag QRE) compared to CB (~ -0.30 V vs Ag QRE). The CVs suggest significant ORR activity of Fe-N/C catalysts in [dema][TfO] and that the presence of Fe plays a significant role towards the ORR activity of the Fe-N/C catalyst. Previous studies have reported strong dependence of ORR activity on Fe^{2+}/Fe^{3+} redox transitions. The lowest onset potential (0.50 V vs Ag QRE) for ORR in [dema][TfO] was observed using a Pt/C catalyst, in agreement with earlier studies using Pt/C in [dema][TfO].

The electrocatalytic activity of Fe-N/C was further studied using RDE voltammetry at rotation speeds ranging from 100 rpm to 1600 rpm in O_2 saturated [dema][TfO], Figure 2a, and compared to commercial Pt/C. The onset and half-wave potentials of Fe-N/C (~ 0.235 V and

0.165 V vs Ag QRE), Figure 2a, are more negative than Pt/C (0.50 V and 0.375 V vs Ag QRE, Figure 8a). Nevertheless, the limiting current density obtained at the Fe-N/C catalyst is to the same as Pt/C. It has been reported that the ORR using Pt in [dema][TfO] proceeds via a $4e^-$ reduction mechanism at the Pt electrodes. These results suggest that the ORR using Fe-N/C in [dema][TfO] also proceeds via a $4e^-$ reduction pathway.

The number of electrons transferred and the electron transfer mechanism for Fe-N/C and Pt/C were further investigated by the RDE measurements according to Koutecky-Levich equation. Figure 2b show the corresponding Koutecky-Levich plots obtained for Fe-N/C at different potential ranges. The plot shows good linearity and almost parallelism of best linear fits, indicating the first order reaction kinetics of dissolved oxygen and similar number of electrons transferred at different potentials. The number of electrons transferred (n) per O_2 molecule of Fe-N/C catalyst calculated from the slopes of linear fits of the Koutecky-Levich plots is 3.78 from -0.20 V to -0.40 V, consistent with a four electron pathway reduction of O_2 to H_2O. Similar results are obtained for Pt/C catalyst where the slopes remains approximately the same and the number of electrons transferred calculated is 4 in the potential range from 0.00 V to 0.20 V, Figure 8b. All the the calculation and all related parameters and their values are presented in Example 1.

To confirm that H_2O is a major product of the ORR, RRDE measurements were carried out to quantify the yield of H_2O_2 during the ORR. To find out the potential where the oxidation of H_2O_2 in [dema][TfO] occurs, a CV in [dema][TfO] containing 50 mM H_2O_2 was carried out at a Pt electrode. Figure 9 shows the CVs at Pt in Ar saturated [dema][TfO] in the absence and presence of 50 mM H_2O_2. The H_2O_2 oxidation peak appears at 0.90 V vs Ag QRE in 50 mM H_2O_2/[dema][TfO] and the shape of the CV is akin to that reported previously in [dema][TfO].

Figure 2c shows the RRDE measurements for Fe-N/C and Pt/C disk electrode and Pt ring electrode in O_2 saturated [dema][TfO] at 1600 rpm while Figure 2d shows the potential dependent variation in % H_2O_2. For Fe-N/C, the H_2O_2 yield remains below 5 % while n calculated

is almost constant at 4 over the whole potential range from -0.185 V to -0.70 V, indicating that H_2O is the main product during the O_2 reduction in [dema][TfO] at the Fe-N/C catalyst. This is in agreement with the number of electrons transferred from RDE measurements using Koutecky-Levich plots. For Pt/C, the % H_2O_2 yield is estimated to be below 4 % and *n* is 4 from 0.085 V to -0.270 V. The procedure to estimate the H_2O_2 yield is presented in Example 1. Both RDE and RRDE results demonstrate high catalytic activity and selectivity of Fe-N/C catalyst for ORR, which is similar to the commercially available Pt/C catalyst in [dema][TfO] under the same conditions.

The stability of Fe-N/C in [dema][TfO] was investigated via a chronoamperometric method. Figure 3a shows the chronoamperometric curves of Fe-N/C and Pt/C in O_2 saturated [dema][TfO] at -0.50 V and -0.15 V, respectively. It can be seen that current density of Fe-N/C electrode exhibits a much slower decay than that of Pt/C electrode (Figure 3a). After 6 hours only a 30 % decrease in current density of the Fe-N/C electrode is observed. By comparison, the Pt/C electrode displays a noticeable decay in activity (75 % loss in initial current density) over a period of 6 hours in [dema][TfO], presumably due to oxide formation and adsorption of $[TfO]^-$ on the surface of the Pt electrode. Previous studies have suggested that the adsorption of low valence state sulfur-containing species, such as SO_3^{2-} and S^{2-}, are poisonous for Fe-N/C catalysts. However, such poisoning effect is much less than that of a Pt-based catalyst. The long term stability of the Fe-N/C catalyst in [dema][TfO] thus could be attributed to the reduced adsorption and/or poisoning effect of $[TfO]^-$ anions on Fe-N/C catalyst surface.

Tolerance to methanol is a notable factor when evaluating the performance of an ORR catalyst due to the poisoning of catalyst by methanol crossover. Therefore, the stability of Fe-N/C and Pt/C in the presence of methanol in O_2 saturated [dema][TfO] was also examined. Figure 3b shows the chronoamperometric measurements carried out at Fe-N/C and Pt/C in O_2 saturated [dema][TfO] containing 3 M CH_3OH at -0.50 V and -0.15 V for 6 hours. A slight increase in current is observed for both Fe-N/C and Pt/C with the

addition of methanol. Enhanced current of ORR in ILs with addition of weak proton source like methanol has been previously reported. However, contribution from methanol oxidation reactions cannot be ignored. The decrease in the current density of Fe-N/C catalyst with the addition of 3 M methanol in [dema][TfO] is ~24 % after 6 hours, which is comparable to ORR in [dema][TfO] without methanol (Figure 3a). In contrast, the current density obtained at Pt/C decreased by as much as ~72 %.

These results indicate that the Fe-N/C catalyst has a significantly improved stability and methanol tolerance than the commercial Pt/C for ORR in [dema][TfO].

The results presented above in Example 2 demonstrate that a non-precious metal catalyst in contact with a cathode can effectively reduce oxygen to H_2O via a 4 e^- reduction in a protic ionic liquid. Accordingly, and as will be apparent to a person skilled in the art, these results demonstrate that such a system can be used in a fuel cell comprising a protic ionic liquid.

It is to be understood that, if any prior art publication is referred to herein, such reference does not constitute an admission that the publication forms a part of the common general knowledge in the art, in Australia or any other country.

In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word “comprise” or variations such as “comprises” or “comprising” is 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 invention.

CLAIMS:

1. A fuel cell comprising:

- an anode;

- a cathode;

- a non-precious metal catalyst in contact with the cathode; and

- an electrolyte comprising a protic ionic liquid in contact with the non-precious metal catalyst.

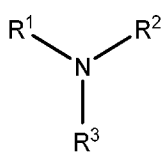
2. The fuel cell according to claim 1, wherein the non-precious metal catalyst is a Fe-N/C catalyst.

3. The fuel cell according to claim 1 or 2, wherein the protic ionic liquid has the formula $(A^-)(BH^+)$, wherein A^- is the conjugate base of acid HA, and BH^+ is the conjugate acid of base B, and the difference in pK_a between HA and BH^+ (ΔpK_a) is between about 12 and about 30.

4. The fuel cell according to claim 3, wherein the ΔpK_a is between about 15 and about 18.

5. The fuel cell according to claim 3 or 4, wherein the base B is an amine.

6. The fuel cell according to any one of claims 3 to 5, wherein the base B is of formula (I):



(I),

wherein R^1, R^2 and R^3 are each independently selected from the group consisting of hydrogen, optionally substituted alkyl (e.g. C_{1-6}alkyl), optionally substituted alkenyl (e.g. C_{2-6}alkenyl), and optionally substituted alkynyl (e.g. C_{2-6}alkynyl);

and wherein R^1, R^2 and/or R^3 are optionally joined to form a saturated or unsaturated optionally substituted heterocycle, a saturated or unsaturated optionally substituted heterobicycle or a saturated or unsaturated optionally substituted heterotricycle.

7. The fuel cell according to claim 5, wherein the base B is a trialkyl amine.

8. The fuel cell according to claim 7, wherein the base B is diethylmethylamine.

9. The fuel cell according to any one of claims 3 to 8, wherein the conjugate base A^- is the conjugate base of a strong acid.

10. The fuel cell according to any one of claims 3 to 9, wherein the conjugate base A^- is non-nucleophilic.

11. The fuel cell according to any one of claims 3 to 10, wherein the conjugate base A^- is triflate (TfO^-).

12. The fuel cell according to any one of claims 1 to 11, wherein the protic ionic liquid is [dema][TfO].

13. The fuel cell according to any one of claims 2 to 12, wherein the Fe-N/C catalyst is derived from p-phenylenediamine, ferric chloride and carbon black.

14. The fuel cell according to any one of claims 1 to 13 comprising a membrane disposed between the anode and cathode, wherein the membrane permits protons to pass through the membrane while inhibiting or impeding the passage or conduction of electrons.

15. Use of a non-precious metal catalyst in a fuel cell to effect the $4e^-$ reduction of O_2 to H_2O in an electrolyte comprising a protic ionic liquid.

16. A method of reducing O_2 to H_2O comprising contacting O_2 and a non-precious metal catalyst in an electrolyte comprising a protic ionic liquid.

17. The reduction of O_2 to H_2O using a non-precious metal catalyst in an electrolyte comprising a protic ionic liquid.

18. An electrode for use in a fuel cell comprising an electrolyte comprising a protic ionic liquid, the electrode having a non-precious metal catalyst on its surface.

19. A half-cell for a fuel cell comprising an electrode having a non-precious metal catalyst on its surface, wherein the electrode is in contact with a protic ionic liquid.

20. The use according to claim 15, method according to claim 16, reduction according to claim 17, electrode according to claim 18 or half-cell according to claim 19, wherein the non-precious metal catalyst is a Fe-N/C catalyst.

21. The use, method, reduction, electrode or half-cell according to claim 20, wherein the protic ionic liquid has the formula $(A^-)(BH^+)$, wherein A^- is the conjugate base of acid HA, and BH^+ is the conjugate acid of base B, and the difference in pK_a between HA and BH^+ (ΔpK_a) is between about 12 and about 30.

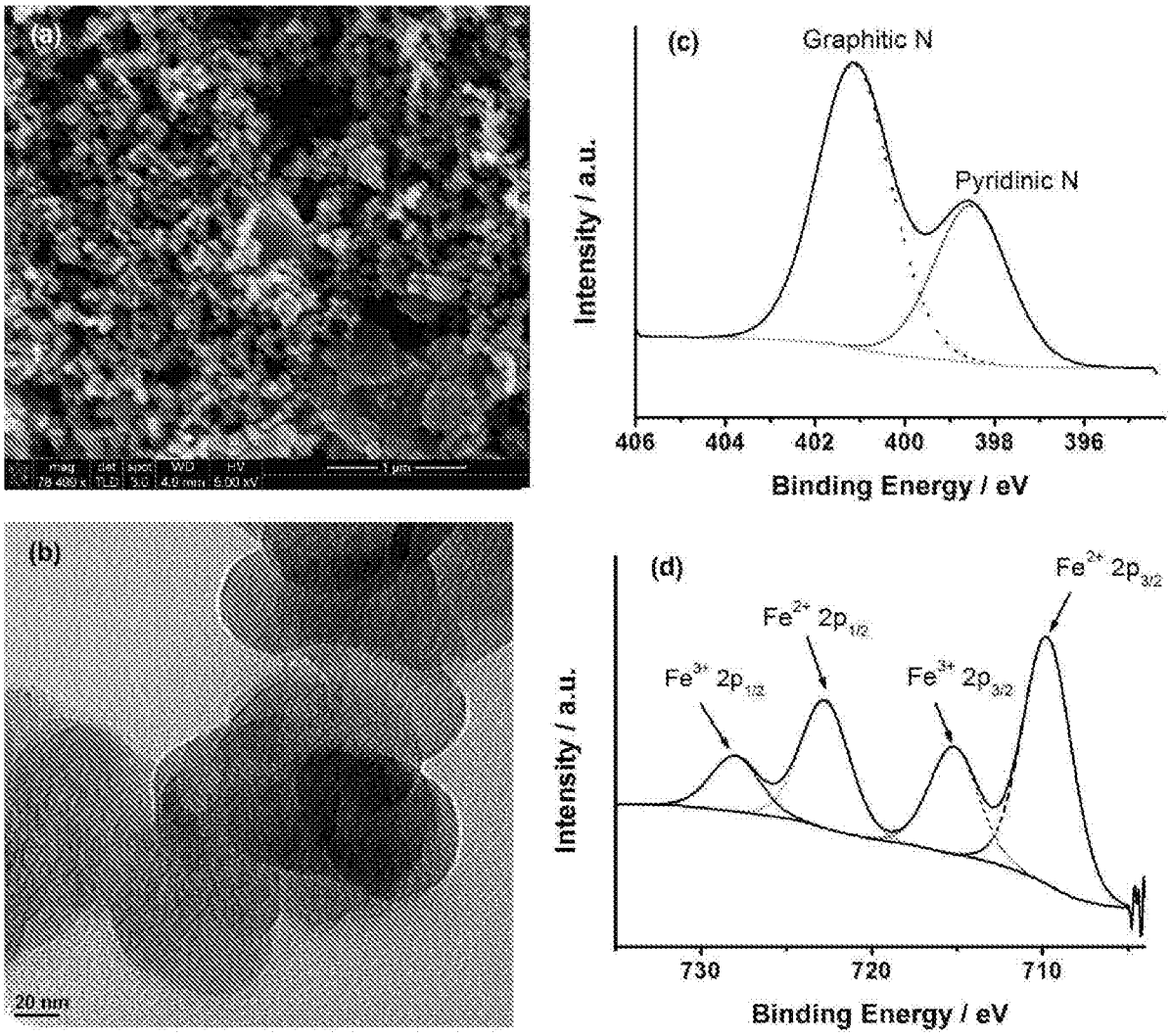

(a)
(b)
20 nm
(c)
Graphitic N
Pyridinic N
Intensity / a.u.
406
404
402
400
398
396
Binding Energy / eV
(d)
Fe2+ 2p3/2
Fe2+ 2p1/2
Fe3+ 2p1/2
Fe3+ 2p3/2
Intensity / a.u.
730
720
710
Binding Energy / eV

Figure 1.

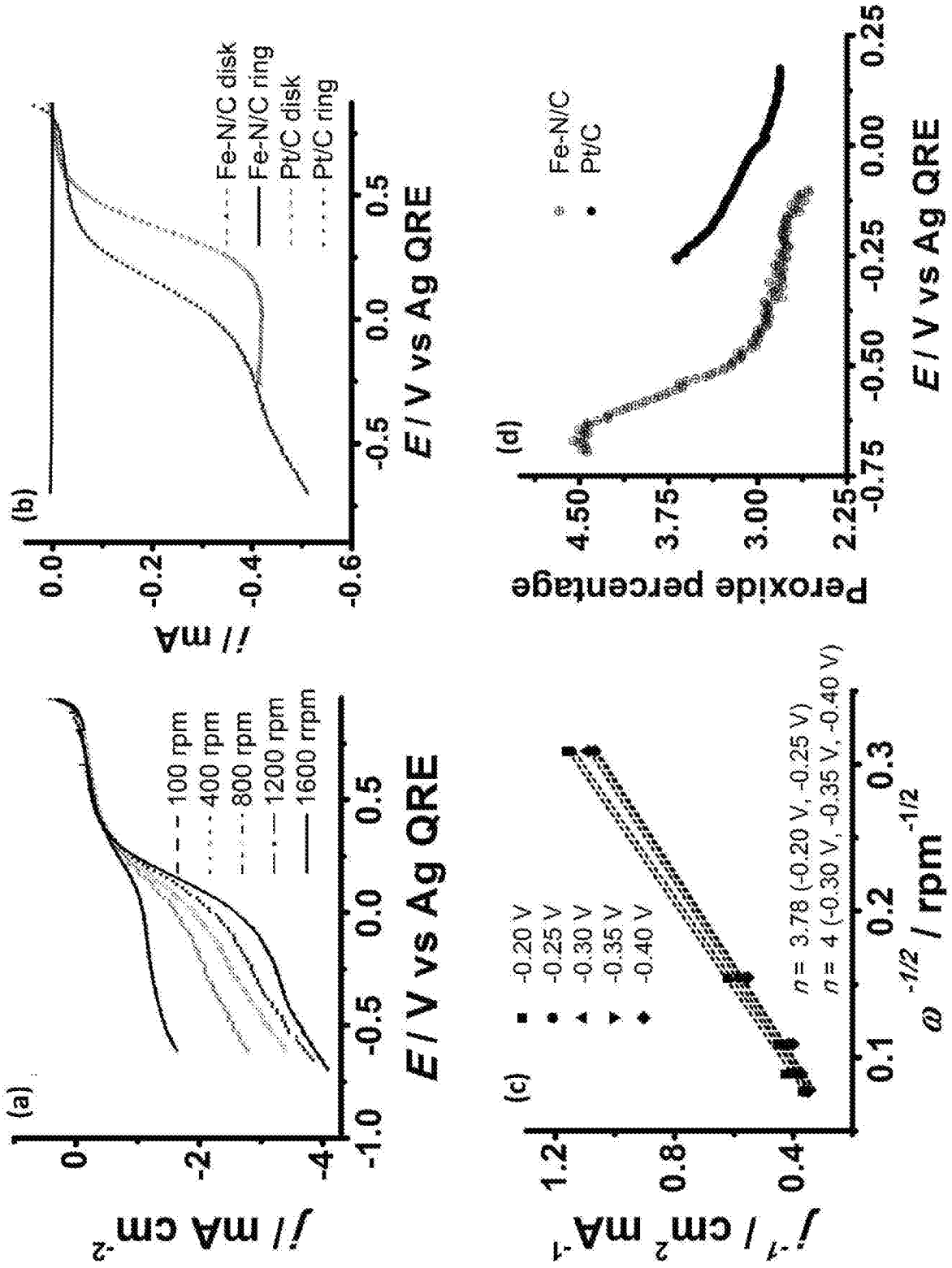

(a)
100 rpm
400 rpm
800 rpm
1200 rpm
1600 rrpm
j / mA cm-2
E / V vs Ag QRE
(b)
Fe-N/C disk
Fe-N/C ring
Pt/C disk
Pt/C ring
i / mA
E / V vs Ag QRE
(c)
-0.20 V
-0.25 V
-0.30 V
-0.35 V
-0.40 V
n = 3.78 (-0.20 V, -0.25 V)
n = 4 (-0.30 V, -0.35 V, -0.40 V)
j-1 / cm2 mA-1
ω-1/2 / rpm-1/2
(d)
Fe-N/C
Pt/C
Peroxide percentage
E / V vs Ag QRE

Figure 2.

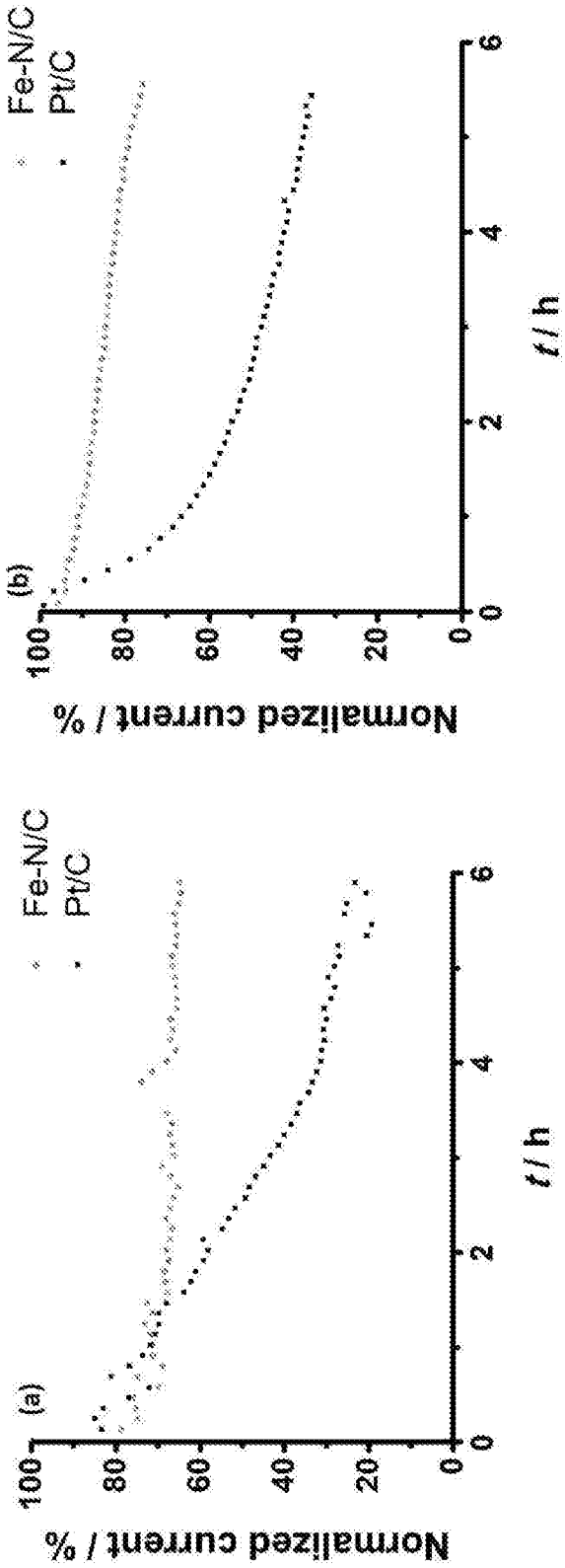

(b)
Fe-N/C
Pt/C
Normalized current / %
100
80
60
40
20
0
0
2
4
6
t / h
(a)
Fe-N/C
Pt/C
Normalized current / %
100
80
60
40
20
0
0
2
4
6
t / h

Figure 3.

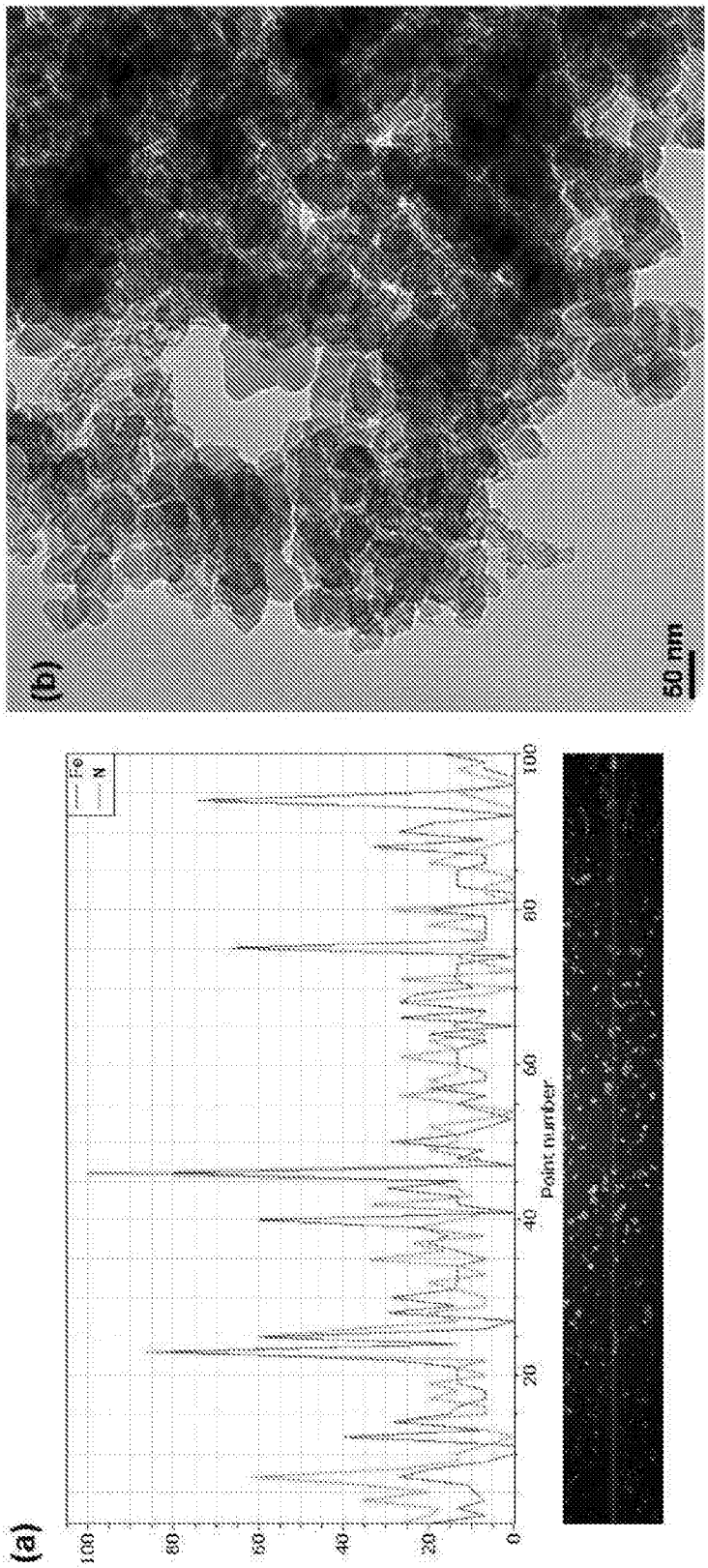


Figure 4.

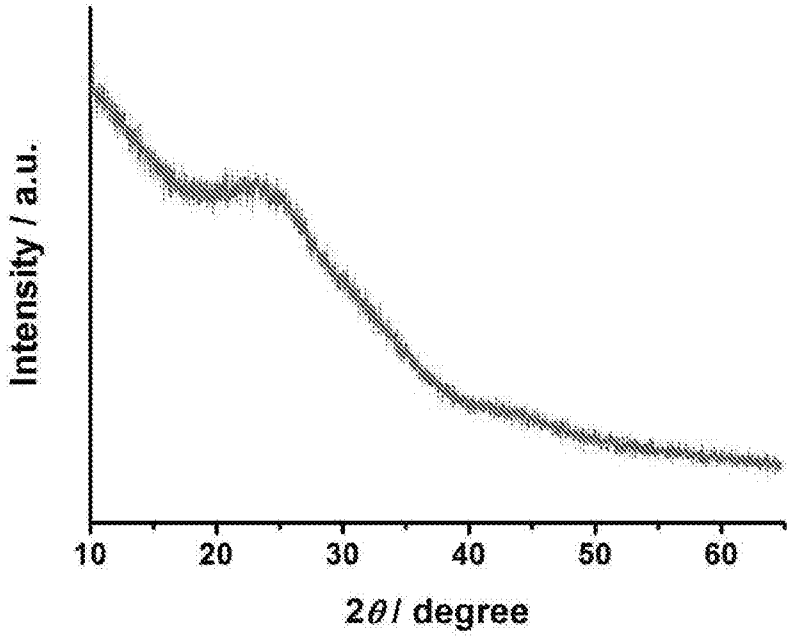


Figure 5.

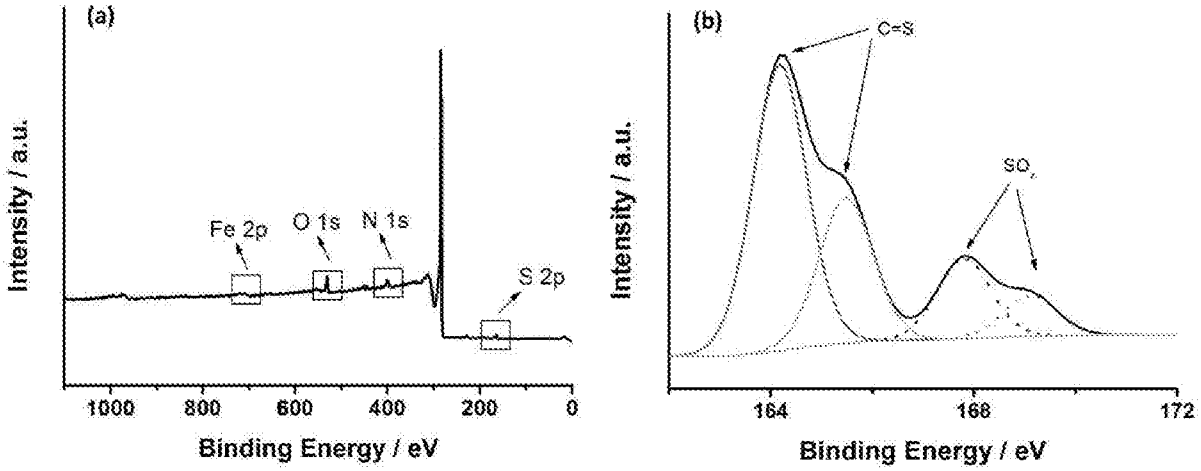


Figure 6.

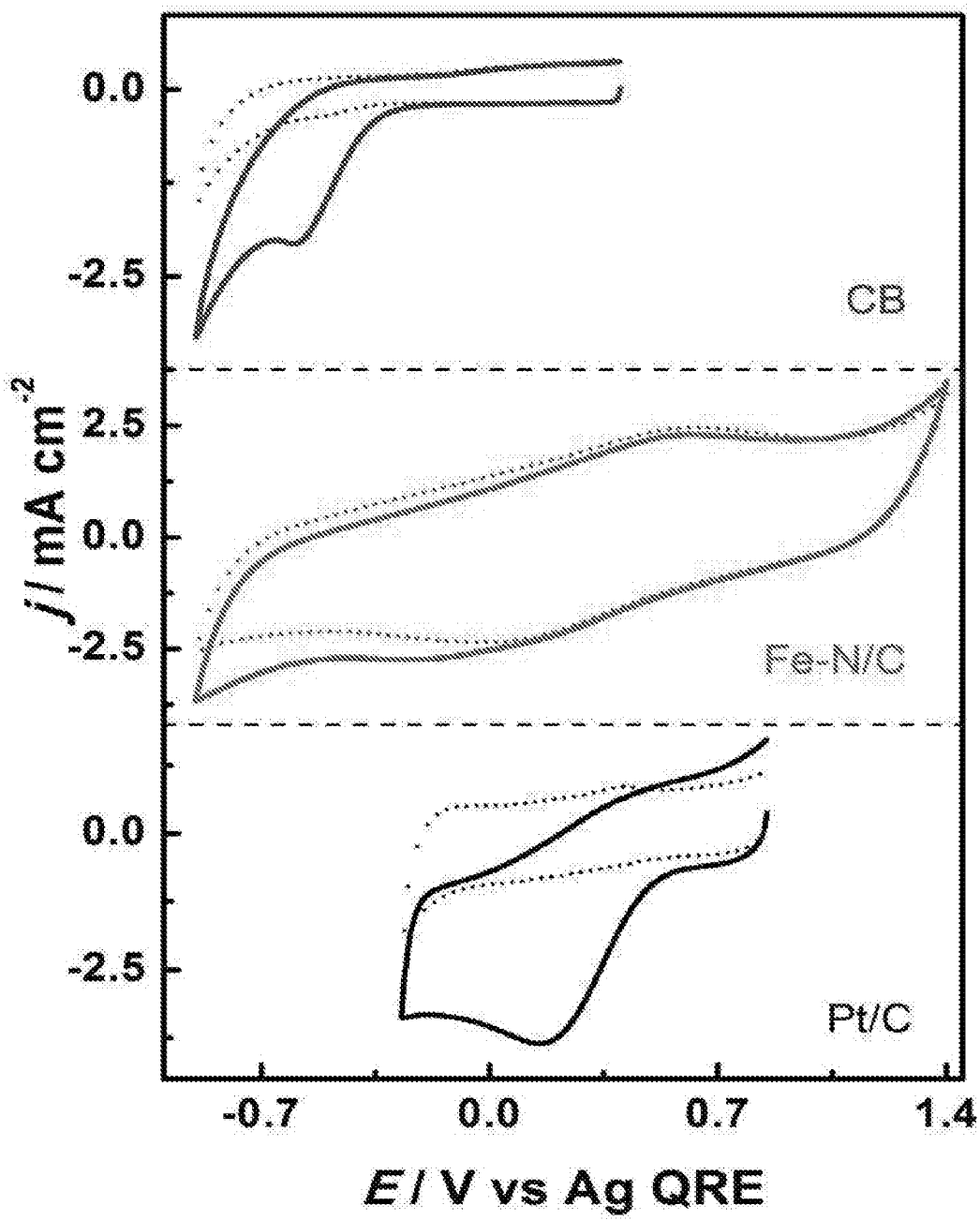


Figure 7.

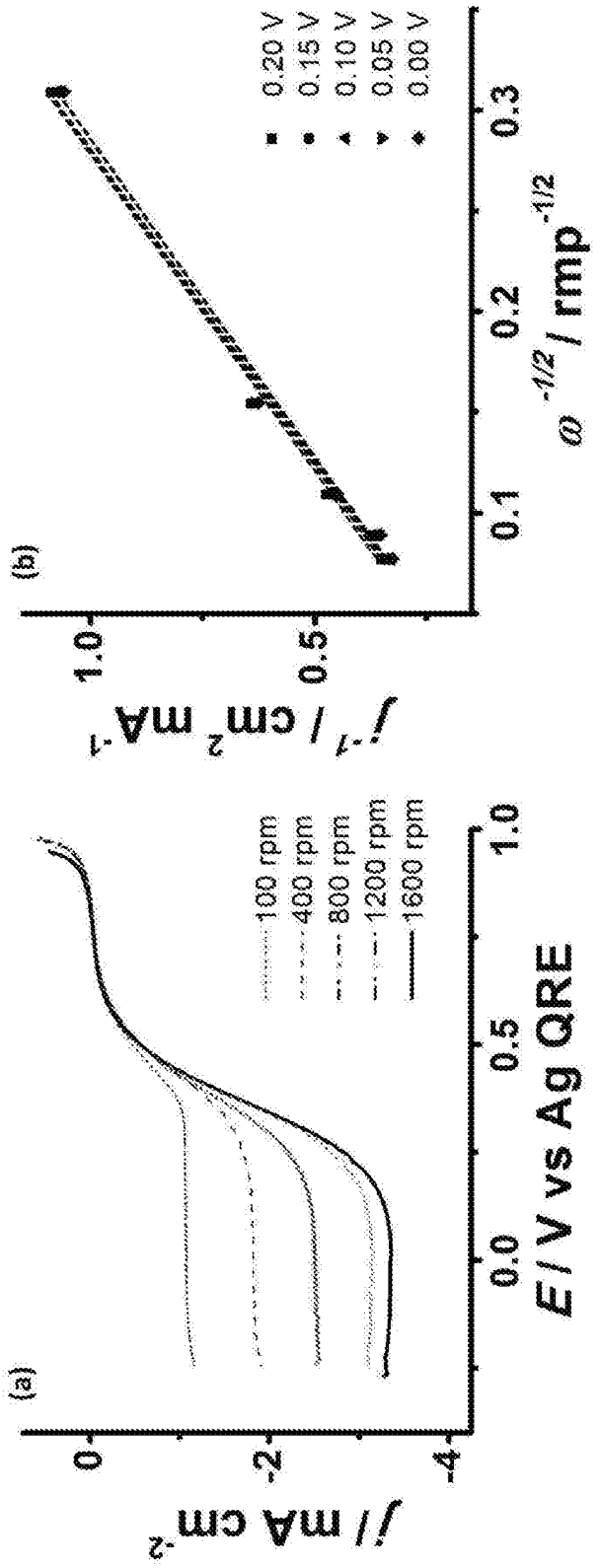

(a)
j / mA cm-2
0
-2
-4
0.0
0.5
1.0
E / V vs Ag QRE
100 rpm
400 rpm
800 rpm
1200 rpm
1600 rpm
(b)
j-1 / cm2 mA-1
1.0
0.5
0.1
0.2
0.3
ω-1/2 / rmp-1/2
0.20 V
0.15 V
0.10 V
0.05 V
0.00 V

Figure 8.

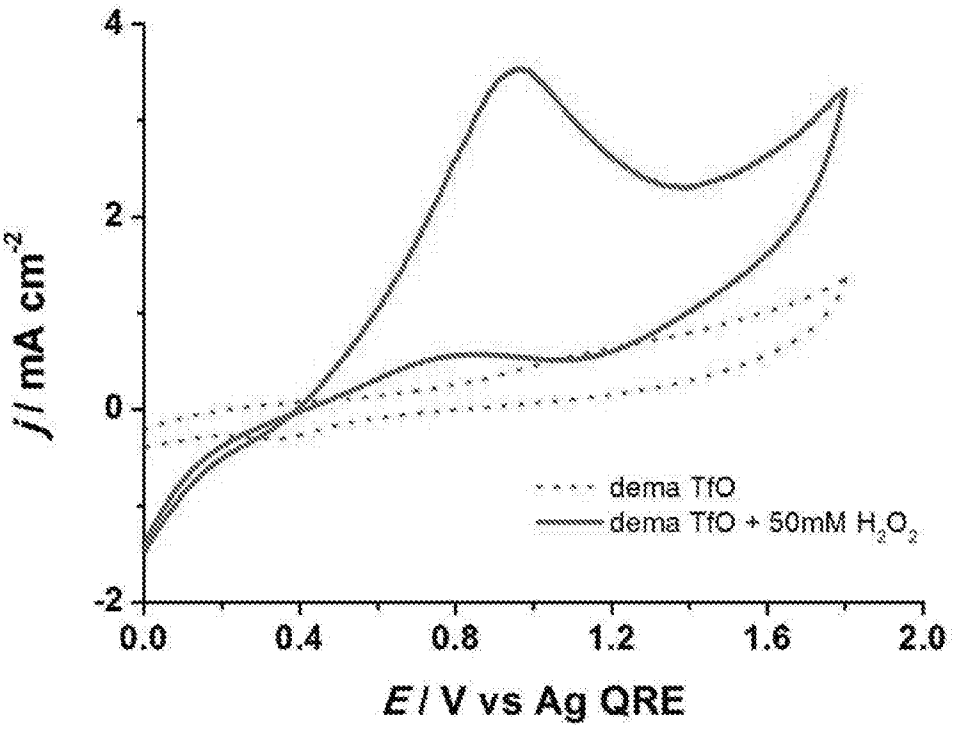

4
2
0
-2
0.0
0.4
0.8
1.2
1.6
2.0
j / mA cm-2
E / V vs Ag QRE
dema TfO
dema TfO + 50mM H2O2

Figure 9.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2017/050891

A. CLASSIFICATION OF SUBJECT MATTER

H01M 4/90 (2006.01) H01M 8/02 (2016.01)

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)

PATENW, Google Patents, Espacenet: IPC & CPC (H01M8/LOW, H01M12/06/LOW, H01M12/08/LOW, H01M16/LOW, H01M2250/LOW, Y02E60/50/LOW, B01J23/745, B01J23/862, B01J23/881, B01J23/94, B01J27/1853, B01J29/0333, B01J31/403, H01M8/14, H01M8/244, H01M2300/0022, H01M2300/0045, H01M2300/0048, Y02E60/526/LOW, H01M4/90/LOW)
PATENW, Google Patents, Google Internet, Google Scholar, Espacenet, STN (databases: CAplus, DWPI, BIOSIS, MEDLINE, INSPEC, INPADOC, AUPATFULL, CANPATFULL, CNFULL, DEFULL, EPFULL, FRFULL, GBFULL, INFULL, JPFULL, KRFULL, PCTFULL, USFULL): Keywords (Chuan, Zhao, fuel, cell, proton, exchange, membrane, catalyst, non-precious, iron, Fe-N/C, M-N/C, Fe(III), ferric, chloride, protic, ionic, liquid, PIL, diethylmethylammonium, dema, triflate, TfO, trifluoromethanesulfonate, [dema][TfO], phenylenediamine, para, carbon, black and like terms in various combinations)
STN (databases: CAS Registry and CAplus): Registry search based on CAS numbers 7705-08-0, 10025-77-1, 106-50-3, 1333-86-4; references related to CAS numbers viewed in CAplus
Applicant and Inventor names searched in Espacenet, AusPat and internal databases provided by IP Australia.

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	

[X] Further documents are listed in the continuation of Box C [X] 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	Date of mailing of the international search report
7 November 2017	07 November 2017
Name and mailing address of the ISA/AU	**Authorised officer**
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au	Andrew Rapson AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. +61262832624

INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. **PCT/AU2017/050891**
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 2011/0281184 A1 (FRIESEN ET AL.) 17 November 2011 Paragraphs 0006-0007, 0014, 0034-0036, 0045, 0068-0069, 0097-0106; Figure 3 As above	1, 3-12, 15-19 2, 13, 20-21
X Y	US 2007/0259236 A1 (LANG ET AL.) 08 November 2007 Abstract; paragraphs 0036, 0038, 0054-0055, 0093; Figures 1-4 As above	1, 3, 5-6, 9, 14, 18-19 2, 13, 20-21
Y	US 2014/0302407 A1 (KOGAN ET AL.) 09 October 2014 Abstract; paragraphs 0021, 0031, 0041; claim 20	2, 13, 20-21
Y	CN 103326041 A (UNIV XIAMEN) 25 September 2013, Bibliographic information retrieved from Espacenet, specification machine translated using Google Patents Abstract; paragraphs 0007, 0010, 0012	2, 13, 20-21
X	US 2014/0220459 A1 (SONY CORPORATION) 07 August 2014 Paragraphs 0046, 0085-0094, 0098-0101, 0108, 0124-0141; Figures 8A-8B, 13, 15-16	1-21

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2017/050891**

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 2011/0281184 A1	17 November 2011	US 2011281184 A1	17 Nov 2011
		US 9184478 B2	10 Nov 2015
		AU 2010247863 A1	24 Nov 2011
		AU 2010247863 B2	03 Dec 2015
		BR PI1014534 A2	05 Apr 2016
		CA 2761084 A1	18 Nov 2010
		CN 102742069 A	17 Oct 2012
		CN 102742069 B	25 Nov 2015
		CN 102971904 A	13 Mar 2013
		CN 102971904 B	08 Jun 2016
		EP 2430698 A1	21 Mar 2012
		EP 2430698 B1	06 Jul 2016
		EP 2569819 A1	20 Mar 2013
		JP 2012527090 A	01 Nov 2012
		JP 5986505 B2	06 Sep 2016
		JP 2013530494 A	25 Jul 2013
		JP 2017027948 A	02 Feb 2017
		TW 201112467 A	01 Apr 2011
		TW I484683 B	11 May 2015
		US 2010285375 A1	11 Nov 2010
		US 8895197 B2	25 Nov 2014
		US 2016049667 A1	18 Feb 2016
		WO 2010132357 A1	18 Nov 2010
		WO 2011143368 A1	17 Nov 2011
		ZA 201107794 B	27 Feb 2013
US 2007/0259236 A1	08 November 2007	US 2007259236 A1	08 Nov 2007
		EP 2033257 A2	11 Mar 2009
		JP 2009535790 A	01 Oct 2009
		WO 2008054858 A2	08 May 2008
US 2014/0302407 A1	09 October 2014	US 2014302407 A1	09 Oct 2014
		US 9502717 B2	22 Nov 2016
CN 103326041 A	25 September 2013	CN 103326041 A	25 Sep 2013
		CN 103326041 B	25 Mar 2015
US 2014/0220459 A1	07 August 2014	US 2014220459 A1	07 Aug 2014

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2017/050891**

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 9647305 B2	09 May 2017
		CN 103972521 A	06 Aug 2014
		JP 2014154225 A	25 Aug 2014
		US 2017237135 A1	17 Aug 2017
		US 9793587 B2	17 Oct 2017

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.