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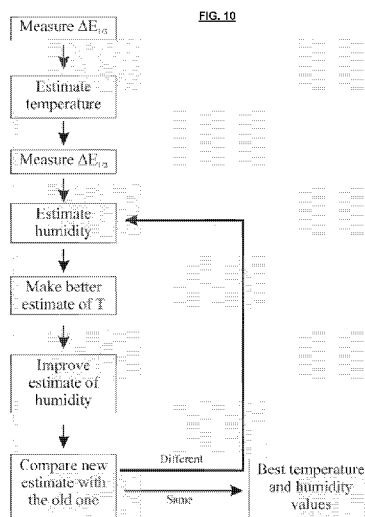
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(54) Title: ELECTROCHEMICAL HUMIDITY AND OPTIONAL TEMPERATURE MEASUREMENT



(57) **Abstract:** Voltammetric method for measuring humidity of the mixture of a ferrocene compound containing a single iron atom and a multiferrocene compound, the method comprising • determining, at a humidity of interest, a first peak potential at which a first electrochemical reaction of the mixture of a ferrocene compound containing a single iron atom and a multiferrocene compound occurs; • determining, at the humidity of interest, a second peak potential at which a second electrochemical reaction of that mixture occurs; • determining the difference between the first and second peak potentials; • converting the difference between the first and second peak potentials to a value of humidity. • Also provided is an electrochemical method for measuring both temperature and humidity simultaneously. Also further provided is a humidity sensor for carrying out these methods, and a voltammetric sensor for sensing a species, the sensor comprising a ferrocene compound containing a single iron atom, a multiferrocene compound and an ionic liquid.

Electrochemical humidity and optional temperature measurement

Field of the Invention

5 The present invention relates to methods and devices for electrochemical measurement of humidity, and if desired, temperature, which can be used in the electrochemical sensing of gases, biological molecules, and other species.

Background

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Electrochemistry finds increasingly wide use in sensors and transducers (see references 1-3 at the end of the description, which are incorporated herein by reference in their entirety), which convert physical or chemical quantities into readable signals. Electrochemical sensors or transducers are normally amperometric or voltammetric in
15 nature where the most well known examples are gas amperometric sensors and pH sensors (see references 4-7 at the end of the description, which are incorporated herein by reference in their entirety). Compared with other types of sensors, electrochemical sensing systems benefit from high reproducibility and low cost. The sought signals for both types of electrochemical sensors are produced by electron transfer process at the
20 electrode/solution interface. Electron transfer is influenced by the local environment due to changed kinetic and thermodynamic properties. Important influential factors include temperature and humidity. However, changes of the temperature or humidity in the surroundings are important to monitor not only in their own right but also because they can indirectly influence the measurement of other properties including the quantification of
25 chemical species.

While current sensors work sufficiently well in many circumstances, they have limitations. For example, while many of the redox reactions that are monitored in the sensors can be sensitive to humidity and temperature changes, the sensors are not necessarily calibrated
30 with humidity or temperature, or even able to monitor humidity or temperature. Even if humidity or temperature is measured, it is typically in a device separate from the electrodes monitoring the various redox reactions. It would be an advantageous to provide an alternative to or an improvement on the current devices.

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Summary of the Invention

In a first aspect, there is provided an electrochemical method for measuring humidity, the method comprising:

- 5 determining, at a humidity of interest, a first potential at which a first electrochemical reaction occurs;
- determining, at the humidity of interest, a second potential at which a second electrochemical reaction occurs;
- determining the difference between the first and second potentials;
- 10 converting the difference between the first and second potentials to a value of humidity.

In a second aspect, an electrochemical method for measuring temperature and humidity, the method comprising the electrochemical method for measuring humidity according to

- 15 the first aspect,
- and further comprising an electrochemical method for measuring temperature comprising:
- determining, at a temperature of interest, a third potential at which a third electrochemical reaction occurs;
- 20 determining, at the temperature of interest, a fourth potential at which a fourth electrochemical reaction occurs;
- determining the difference between the third and fourth potentials;
- converting the difference between the third and fourth potentials to a value of temperature.

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In a third aspect, there is provided a humidity sensor, wherein the sensor is adapted to:

- determine, at a humidity of interest, a first potential at which a first electrochemical reaction occurs;
- determine, at the humidity of interest, a second potential at which a second
- 30 electrochemical reaction occurs;
- determine the difference between the first and second potentials;
- convert the difference between the first and second potentials to a value of humidity.

In a fourth aspect, there is provided an electrochemical sensor for sensing a species, the

35 sensor comprising:

a working electrode, a counter electrode and a carrier medium in contact with the working electrode and the counter electrode, wherein the carrier medium contains, and/or the working electrode has immobilised on a surface thereof, a ferrocene compound containing a single iron atom and a multiferrocene compound, and the carrier medium is
5 an ionic liquid having a dynamic viscosity, as measured at 20 °C, of at least 50 cP.

The present inventors have developed a method that can measure humidity using electrochemistry. The method can also involve the electrochemical detection of temperature and, if desired, an iterative technique to improve the calculation of the
10 humidity and/or temperature. The method allows the humidity and, if desired, temperature, in the environment around electrochemical systems to be determined, which is useful in many situations. For example, in an electrochemical gas sensor the ambient humidity, and, if desired, the temperature, around the sensor can be directly monitored using the working electrode of the sensor. This allows the gas sensor to be accurately
15 self-calibrated to humidity and, if desired, temperature, and/or different electrochemical information to be obtained at different humidities and/or temperatures. The present inventors have found that the difference in potentials between electrochemical reactions can vary with humidity in a quadratic or linear manner, and therefore the difference in potentials can be used to efficiently determine humidity. The present inventors have also
20 developed systems in which the variation of certain potentials is humidity dependent but effectively temperature independent.

Brief Description of the Figures

25 Figures 1 to 7 show the results of certain electrochemical tests carried out relating to the measurement of humidity and temperature. The tests are described in further detail in the Examples below.

Figure 1 shows (a) square wave voltammetric responses for 1 mM decamethylferrocene and 1 mM bisferrocene in [Moepyrr][FAP] at a frequency of 50 Hz, a step potential of 0.1
30 mV, amplitude of 25 mV and over a temperature range of 298-318 K; and (b), from top to bottom, the corresponding plots of the peak difference of peaks 1 and 3, $\Delta E_{1/3}$, peaks 1 and 2, $\Delta E_{1/2}$ and peaks 2 and 3 $\Delta E_{2/3}$ against temperature.

Figure 2 shows (a) square wave voltammograms for the oxidation of decamethylferrocene and bisferrocene in [Moepyrr][FAP] in the dried air (Relative humidity (RH) = 1%); and (b)-(d) plots of the peak difference of peaks 1 and 2, $\Delta E_{1/2}$, peaks 1 and 3, $\Delta E_{1/3}$ and peaks 2 and 3, $\Delta E_{2/3}$ against temperature respectively.

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Figure 3 shows (a) plots of $\Delta E_{1/2}$ as a function of temperature over the RH range of 1% to 50%; and (b) plots of $\Delta E_{1/3}$ as a function of temperature over the RH range of 1% to 50%.

Figure 4 shows square wave voltammetric responses for decamethylferrocene and bisferrocene in [Moepyrr][FAP] at RH of 1%, 12%, 29%, 35% and 50% and temperature was fixed at 298K. The potential is measured relative to the peak potential for DmFc/DmFc⁺. The inlays show enlargements of the first (left) and second oxidation (right) of bisferrocene.

Figure 5 shows the dependence of $\Delta E_{1/2}$ on the value of RH.

Figure 6 shows the dependence of $\Delta E_{1/3}$ on RH at 298 K, 303 K, 308 K, 313 K and 318 K.

Figure 7 shows the dependence of average $\Delta E_{1/3}$ on the value of RH at 298 K, 303 K, 308 K, 313 K and 318 K.

Figure 8 shows, from top to bottom, the structures of decamethylferrocene and of bisferrocene.

Figure 9 shows the structure of 1-(2-methoxyethyl)-1-methyl-pyrrolidinium tris(pentafluoroethyl)trifluorophosphate ([Moepyrr][FAP]).

Figure 10 shows schematically an example of an iterative method for determining temperature and humidity simultaneously.

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Detailed Description

The present invention provides the first to the fourth aspects mentioned above. Optional and preferred features of the various aspects are described below. Unless otherwise

stated, any optional or preferred feature may be combined with any other optional or preferred feature, and with any of the aspects of the invention mentioned herein.

The method involves determining, at a humidity of interest, a first potential at which a first electrochemical reaction occurs, and then

determining at the humidity of interest a second potential at which a second electrochemical reaction occurs.

Optionally, the method additionally involves determining, at a temperature of interest, a third potential at which a third electrochemical reaction occurs, and then

determining, at the temperature of interest, a fourth potential at which a fourth electrochemical reaction occurs.

The first electrochemical reaction is different from the second electrochemical reaction, such that a difference in potential can be observed. Likewise, if carried out, the third electrochemical reaction is different from the fourth electrochemical reaction.

Optionally, the first electrochemical reaction and third electrochemical reaction are the same as one another. This allows a single reaction to be used as a reference reaction, giving a single potential against which the second potential and fourth potentials can be compared, in the determination of humidity and temperature, respectively.

Typically, the second electrochemical reaction and fourth electrochemical reactions are different to one another.

The humidity is preferably that of the environment, which may be ambient air, around the electrochemical device being used to carry out the method described herein and/or the sensor described herein. If the first and second reactions are carried out in a carrier medium, the humidity may be that of any gas, e.g. air, in contact with the carrier medium.

The humidity is preferably relative humidity, which may be as defined in equation A :

$$RH (\%) = \frac{e_w}{e_w^*} \times 100 \quad \text{equation A,}$$

wherein e_w is the partial pressure of water vapour (H₂O) in a sample of interest and e_w^* is the saturated vapor pressure of

water at a prescribed temperature for the sample of interest.

Preferably, the difference between the first and second potentials varies with a variation in humidity, but is substantially independent or independent with changes in temperature. "Substantially independent with changes in temperature" indicates that the gradient of the difference between the first and second potentials (in V) with temperature (in K) at a fixed
5 humidity is 1×10^{-4} or less, optionally 1×10^{-5} or less, optionally 1×10^{-6} or less, optionally 5×10^{-7} or less, for example over at least some, optionally all, of the temperature range of from 298 to 318 K.

Preferably, the first and second potentials are measured at the same working electrode.

10 Preferably, the first, second, third and fourth potentials are measured at the same working electrode. This allows for an efficient measurement of both humidity and temperature in the same device, which may be a sensor as described herein, and allows, if desired, any other electrochemical measurements and/or calculations being made in the device to take into account the humidity or temperature.

15

In an embodiment, the difference between third and fourth potentials is dependent on humidity and/or the difference in first and second potentials is dependent on temperature, and

(i) the value of temperature initially obtained in accordance with the second aspect is
20 used to recalculate the value of humidity and/or

(ii) the value of humidity initially obtained in accordance with the first aspect is used to recalculate the value of temperature. The recalculated value of humidity may be compared with the value of humidity initially obtained in accordance with the first aspect; and the recalculation repeated if the difference between the recalculated value of humidity
25 and the value of humidity initially obtained is not below a predetermined threshold. The recalculation may be repeated until the difference between two consecutively obtained recalculated values of humidity is below a predetermined threshold.

In a similar manner, the recalculated value of temperature may be compared with the
30 value of temperature initially obtained in accordance with the second aspect; and the recalculation repeated if the difference between the recalculated value of temperature and the value of temperature initially obtained is not below a predetermined threshold.

In an embodiment, the difference between third and fourth potentials is dependent on humidity, and the electrochemical method for measuring temperature is carried out a first time in which the converting of the difference between the third and fourth potentials to a value of temperature uses a relationship between known temperatures and the difference between third and fourth potentials at an predetermined humidity to obtain a first value in temperature,

and the measured value of humidity obtained in the electrochemical method in accordance with the first aspect is then used to recalculate the value of temperature, using a relationship between known temperatures and the difference between third and fourth potentials at the measured value of humidity,

and the first value in temperature and recalculated value of temperature are compared with one another.

In an embodiment, the difference between first and second potentials is dependent on temperature, and the electrochemical method for measuring humidity is carried out a first time in which the converting of the difference between the first and second potentials to a value of humidity uses a relationship between known humidities and the difference between first and second potentials at an predetermined temperature to obtain a first value in humidity,

and the measured value of temperature obtained in the electrochemical method in accordance with the second aspect is then used to recalculate the value of humidity, using a relationship between known humidities and the difference between first and second potentials at the measured value of humidity,

and the first value in humidity and recalculated value of humidity are compared with one another.

Optionally, in any of the methods described above, the recalculation is repeated until the difference between recalculated values of temperature and/or recalculated values of humidity is/are below a predetermined threshold.

The predetermined threshold may be a percentage difference between the relevant values. The percentage difference may, for example, be 10% or less, optionally 5% or less, optionally 2 % or less, optionally 1% or less, optionally 0.5 % or less.

As mentioned, the method described herein involves first and second electrochemical reactions, and, optionally, third and fourth electrochemical reactions.

The first electrochemical reaction may be an oxidation or a reduction of a first species.

- 5 The second electrochemical reaction may be an oxidation or a reduction of a second species. The third electrochemical reaction may be an oxidation or a reduction of a third species. The fourth electrochemical reaction may be an oxidation or a reduction of a fourth species. Optionally, all reactions are oxidations, i.e. requiring a positive potential to be applied (relative to an Ag reference electrode) to a working electrode in contact with
10 the first species and/or second species, and optional third and/or fourth species, to effect its/their oxidation. Optionally, all reactions are reductions, i.e. requiring a negative potential to be applied (relative to an Ag reference electrode) to a working electrode in contact with the first species and/or second species, and optional third and/or fourth species, to effect its/their reduction. Optionally, one or more of the reactions is an
15 oxidation and the other(s) is a/reduction(s).

The first and second species, and, if third and fourth electrochemical reactions are carried out, third and fourth species, may be collectively termed "reaction species" herein.

- 20 Optionally, at least one of the reaction species (in some embodiments the second and, if present, the fourth reaction species) is or comprises a mixed valence compound, preferably a mixed valence compound of class II or class III, most preferably of class III, according to the Robin-Day classification. Mixed-valence compounds contain an element that can be present in more than one oxidation state, for example iron that is both in Fe(II)
25 and Fe(III) states. Mixed-valence compounds of class II or class III show distinguishable potentials for the transition between the various oxidation states. Class III show the most distinction between the potentials of the various electrochemical transitions. The Robin-Day classification of mixed-valence compounds can be found, for example, in Inorganic Electrochemistry, Theory, Practice and Application (2003), authored by Piero Zanello and
30 published by Royal Society of Chemistry, e.g. on pages 174 and 175, which is incorporated herein by reference in its entirety.

- In some embodiments, the second and fourth species may comprise a mixed valence compound, wherein the second species is the mixed valence compound in a first oxidation
35 state, and the fourth species is the a mixed valence compound in a second oxidation state

different from the first oxidation state. In some embodiments, the third and fourth reactions are carried out and the second and fourth reaction species are both a mixed valence compound, wherein the second electrochemical reaction involves a transition of the mixed valence compound from a first oxidation state to a second oxidation state, and the fourth electrochemical reaction involves a transition of the mixed valence compound from the second oxidation state to a third oxidation state. The first and third reactions may be the same as one another and/or may involve the oxidation or reduction of a species different from the mixed valence compound in the second and fourth reactions, but in which the same atom or group that is oxidised or reduced in the mixed valence compound in the second and fourth reactions is oxidised or reduced.

Optionally, at least one of the reaction species (in some embodiments the second and, if present, the fourth reaction species) is or comprises an organic compound having two oxidisable or reducible groups or substituents linked via a delocalised electron system.

The organic compound having two oxidisable or reducible groups or substituents linked via a delocalised electron system may be a mixed valence compound. For example, optionally at least one of the reaction species is or comprises an aryl compound having two oxidisable or reducible substituents on one or more rings of the aryl compound. At least one of the reaction species may, for example, comprise a phenyl moiety having two oxidisable or reducible substituents on the phenyl ring or a naphthyl moiety having two oxidisable or reducible substituents on one or both of rings of the naphthyl moiety. The two oxidisable or reducible groups or substituents (before the relevant electrochemical reaction(s) has/have been carried out) may be selected from, for example, =O, N(R)₂ (wherein each R is alkyl, for example C1 to C10 alkyl, for example C1 to C5 alkyl, for example C1 to C3 alkyl, for example methyl, ethyl or propyl), amino, nitro, OH, COOH, -(C=O)H, -(C=O)R (wherein each R is alkyl, for example C1 to C10 alkyl, for example C1 to C5 alkyl, for example C1 to C3 alkyl, for example methyl, ethyl or propyl). At least one of the reaction species may comprise a phenyl compound having two oxidisable or reducible groups or substituents, which may be in the ortho, meta or para positions on the phenyl ring relative to one another, and may be the same as or different from one another. At least one of the reaction species may comprise a phenyl compound having two oxidisable or reducible groups or substituents para to one another, wherein the two oxidisable or reducible groups or substituents (before the relevant electrochemical reaction(s) has/have been carried out) may be selected from, for example, =O, N(R)₂ (wherein each R is alkyl, for example C1 to C10 alkyl, for example C1 to C5 alkyl, for

example C1 to C3 alkyl, for example methyl, ethyl or propyl), amino, nitro, OH, COOH, - (C=O)H, -(C=O)R (wherein each R is alkyl, for example C1 to C10 alkyl, for example C1 to C5 alkyl, for example C1 to C3 alkyl, for example methyl, ethyl or propyl).

- 5 At least one of the reaction species (in some embodiments the second and, if present, the fourth reaction species) may comprise a phenylenediamine, and optionally, the second and fourth species are each the same phenylenediamine, but in different oxidation states. Optionally, the second and, if present, the fourth reaction species is or comprises a phenylenediamine (and optionally, the second and fourth species are each the same phenylenediamine, but in different oxidation states) and the first and, if present third species, may be selected from an aminophenyl. The phenylenediamine may be selected from o- and p-phenylenediamines. The phenyl of the phenylenediamine may be substituted with groups other than amines, which may be selected from, but are not limited to, halogen, alkyl, aryl and alkaryl. The aminophenyl may be phenyl group having a single amino substituent. The phenyl of the aminophenyl group may have one or more further substituents other than the amino substituent, and optionally the one or more further substituents are selected from halogen, alkyl, aryl and alkaryl.

- At least one of the reaction species (in some embodiments the second and, if present, the fourth reaction species), for example, comprise N,N,N',N'-tetramethyl-p-phenylenediamine, and optionally, the second and fourth species are each N,N,N',N'-tetramethyl-p-phenylenediamine in different oxidation states .

- Optionally, the second and, if present, the fourth reaction species is or comprises an organic compound having two oxidisable or reducible groups or substituents linked via a delocalised electron system, which may be as described above, and the first and, if present, third species, may be selected from (i) a different organic compound having two oxidisable or reducible groups or substituents linked via a delocalised electron system wherein optionally the two oxidisable or reducible groups or substituents are the same as in the second and/or, if present, fourth reaction species and (i) an organic compound having one oxidisable or reducible group or substituent linked to a delocalised electron system wherein optionally the one oxidisable or reducible group or substituent is the same as one or both of the two oxidisable or reducible groups or substituents in the second and/or, if present, fourth reaction species.

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At least one of the reaction species (in some embodiments the second and, if present, the fourth reaction species) may be or comprise a quinone. The second and fourth species may, for example, comprise the same quinone, but in different oxidation states. The quinone may have one or more optional substituents on a ring thereof, for example substituents selected from, but not limited to, halogen, alkyl, aryl and alkaryl. The quinone may be selected from a benzoquinone, a naphthoquinone and an anthraquinone. The quinone may be selected from 1,2-benzoquinone, 1,4-benzoquinone, 1,4-naphthoquinone, and 9,10-anthraquinone, and substituted derivatives thereof, for examples derivatives in which at least one hydrogen atom on a ring has been replaced with a substituent selected from halogen, alkyl, aryl and alkaryl. Optionally, the second and, if present, the fourth reaction species is or comprises a quinone, and the first and, if present third species, may be a compound having a carbonyl, which may be a different quinone to that of the second and, if present, the fourth reaction species. Optionally, the second and, if present, the fourth reaction species is or comprises a benzoquinone or naphthoquinone, and the first and, if present, third species, may be an anthraquinone. Optionally, the second and, if present, the fourth reaction species is or comprises an anthraquinone, and the first and, if present, third species, may be a benzoquinone or naphthoquinone.

Optionally, at least one of the reaction species (in some embodiments the second and, if present, the fourth reaction species) is or comprises an organometallic compound having two metal centres, each of which can be oxidised or reduced at a different potential from the other. The two metals of the two metal centre may be the same as or different to one another and selected from, for example, a transition metal, a lanthanide or actinide. In an embodiment, at least one of the reaction species is or comprises a metallocene compound comprising two metal centres. In some embodiments, the second and fourth species may comprise an organometallic compound having two metal centres, each of which can be oxidised or reduced at a different potential from the other, wherein the second species is the organometallic compound having two metal centres in a first oxidation state, and the fourth species is the organometallic compound having two metal centres in a second oxidation state different from the first oxidation state.

Optionally, at least one of the reaction species (in some embodiments the second and, if present, the fourth reaction species) is or comprises a multiferrocene compound. A multiferrocene compound is a compound having a plurality of ferrocene groups, and is

sometimes termed an oligoferrocene compound. Each of the cyclopentadienyl rings of ferrocene groups may have one or more substituents thereon. Each ferrocene group may be linked to another ferrocene group either directly via a covalent bond between a cyclopentadienyl ring of each ferrocene group or via a linker group covalently bonded to cyclopentadienyl ring of each ferrocene group. The multiferrocene compound may be selected from, for example, biferrocene, diferrocenylmethane, 1,2-bis(ferrocenyl)ethane (sometimes termed diferrocenylethane), diferrocenylethene (also termed 1,2-diferrocenylethylene or bisferrocene) and diferrocenylethyne. Multiferrocene compounds are described, for example, in Inorganic Electrochemistry, Theory, Practice and Application (2003), authored by Piero Zanello and published by Royal Society of Chemistry, which is incorporated herein by reference in its entirety. In some embodiments, the second and fourth species may comprise a multiferrocene compound, wherein the second species is the multiferrocene compound in a first oxidation state, and the fourth species is the multiferrocene compound in a second oxidation state different from the first oxidation state. The first and third reactions may be the same as one another and/or may involve the oxidation or reduction of a ferrocene different from the multiferrocene compound in the second and fourth reactions, which may be a ferrocene having a single iron atom.

Optionally, at least one of the reaction species (in some embodiments, the first and, if present, second species) is a ferrocene containing a single iron atom. The ferrocene containing a single iron atom may, be selected from a substituted or unsubstituted ferrocene. Unsubstituted ferrocene may have the formula $\text{Fe}(\text{C}_5\text{H}_5)_2$. In a substituted ferrocene, at least one hydrogen atom in the formula $\text{Fe}(\text{C}_5\text{H}_5)_2$ has been replaced with a substituent. Optionally, in a substituted ferrocene, all hydrogen atoms in the formula $\text{Fe}(\text{C}_5\text{H}_5)_2$ has been replaced with a substituent. The substituent may be a hydrocarbon substituent. The substituent(s) may (each) be independently selected from optionally substituted alkyl, optionally substituted alkoxy, optionally substituted aryl, optionally substituted aralkyl groups. In an embodiment, at least one of the reaction species (in some embodiments, the first and, if present, second species) is a ferrocene of the formula $\text{Fe}(\text{C}_5\text{R}_1\text{R}_2\text{R}_3\text{R}_4\text{R}_5)(\text{C}_5\text{R}_6\text{R}_7\text{R}_8\text{R}_9\text{R}_{10})$, wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_9 and R_{10} are each independently selected from H and a hydrocarbon group. In an embodiment, at least one of the reaction species (in some embodiments, the first and, if present, second species) is a ferrocene of the formula $\text{Fe}(\text{C}_5\text{R}_1\text{R}_2\text{R}_3\text{R}_4\text{R}_5)(\text{C}_5\text{R}_6\text{R}_7\text{R}_8\text{R}_9\text{R}_{10})$, wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_9 and R_{10} are each independently selected from H, optionally

substituted alkyl, optionally substituted alkoxy, optionally substituted aryl, optionally substituted aralkyl groups. In an embodiment, R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_9 and R_{10} are each independently selected from optionally substituted alkyl, optionally substituted alkoxy, optionally substituted aryl, optionally substituted aralkyl groups. In some
5 embodiments, R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_9 and R_{10} are the same group. In an embodiment, R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_9 and R_{10} are each independently selected from optionally substituted alkyl. The alkyl in any of alkyl, optionally substituted alk(yl)oxy, and optionally substituted aralkyl groups may be selected from C1 to C10 alkyl, optionally from C1 to C5 alkyl, optionally from methyl, ethyl, propyl, butyl and pentyl. Alkyl may be
10 branched or straight chain alkyl. In an embodiment, at least one of the reaction species (in some embodiments, the first and, if present, second species) is decamethyl ferrocene.

Optionally, the first electrochemical reaction involves a change in oxidation state of an atom in a first species, and the second electrochemical reaction involves a change in
15 oxidation state of an atom in a second species, with the first and second species being different to one another, and the atoms being oxidised or reduced in first and second species being the same as one another and in the same coordination environment.

If the atoms being oxidised or reduced in first and second species are in the same
20 coordination environment, this may indicate one or more of the following: (i) that the atom being oxidised or reduced in each of the first and second species is bonded to the same number (and optionally type) of other atoms in the first and second species in the same way; (ii) that the atom being oxidised or reduced in each of the first and second species is in the same symmetry environment; (iii) that the first and second species, before being
25 oxidised or reduced in the first and second electrochemical reactions, have the same charge as one another, and both first and second species have the same charge as one another after the first and second electrochemical reactions.

In an embodiment, the atom is iron and first and second species are different ferrocenes,
30 which may each be independently selected from a ferrocene containing a single iron atom, and a multiferrocene compound. In an embodiment, if the iron in each of the ferrocenes of the first and second species is in the same coordination environment, this may indicate that the ferrocenes of the first and second species, before being oxidised or reduced in the first and second electrochemical reactions, have the same charge as one
35 another, and both ferrocenes of first and second species have the same charge as one

another after the first and second electrochemical reactions. In an embodiment, the first species is a ferrocene containing a single iron atom, and the second species is a multiferrocene compound, and the first electrochemical reaction is the oxidation of iron from Fe(II) to Fe(III), and the second electrochemical reaction is the first oxidation of the multiferrocene compound in which one of the iron atoms is oxidised from Fe(II) to Fe(III).
5 The first oxidation may be an oxidation of the multiferrocene compound in which all iron atoms are in the Fe(II) state.

Optionally, the change of oxidation state of the atom in the first and second
10 electrochemical reactions is from a first oxidation state to a second oxidation state, the first oxidation state is the same in the first and second electrochemical reactions, and the second oxidation state is the same in the first and second electrochemical reactions, and preferably the first and second species, before being oxidised or reduced in the first and second electrochemical reactions, have the same charge as one another, and, after the
15 first and second electrochemical reactions, both first and second species have the same charge as one another. In some embodiments, the first and second species are both metallocenes, and the atom being oxidised or reduced in first and second reactions may be a metal. In some embodiments, the first and second species are both ferrocenes, and the atom being oxidised or reduced in first and second reactions is iron. The present
20 inventors have found that the difference in potential between certain reactions can be dependent on changes in humidity, but substantially independent of changes of temperature. The above-stated conditions for the atom being oxidised or reduced in the first and second species seem to promote low temperature dependence of the potential difference.

25 Optionally, the first and third electrochemical reactions are the same as one another, and the fourth electrochemical reaction involves further oxidation or reduction of the species produced by the oxidation or reduction of the second species in the second electrochemical reaction. Optionally, the first species comprises a ferrocene containing a
30 single iron atom, and the second species comprises a multiferrocene compound.

In an embodiment, the first species and third species are a ferrocene containing a single iron atom, and the second and third species are a multiferrocene compound, and the first and third electrochemical reactions are the oxidation of iron (in the ferrocene containing a
35 single iron atom) from Fe(II) to Fe(III), and the second electrochemical reaction is the first

oxidation of the multiferrocene compound in which one of the iron atoms is oxidised from Fe(II) to Fe(III), and the fourth electrochemical reaction is the second or subsequent oxidation of the multiferrocene compound. The first oxidation may be an oxidation of the multiferrocene compound in which all iron atoms are in the Fe(II) state, and the second
5 oxidation may be the oxidation of the multiferrocene compound produced in the first oxidation (such that the species being oxidised in the second oxidation has one Fe(III) atom, with the remaining iron atom or atoms in the multiferrocene being Fe(II)).

The potential of the first and second, and, if carried out, third and fourth, electrochemical
10 reactions may be measured by any suitable technique. Typically, first and second potentials (and, if third and fourth electrochemical reactions are carried out, third and fourth potentials) are measured using a voltammetry technique, which uses a working electrode, a counter electrode, and, if desired, a reference electrode. A potential may be applied between the working electrode and counter electrode, and the resulting current
15 measured, using a potentiostat. The potential at which each of the first and second, and optional third and fourth, electrochemical reactions occurs may be the electrode potential of each of first, second, third and fourth electrochemical reactions, respectively. The electrode potential of any of the electrochemical reactions may be determined using any suitable technique. The potential at which each of the first and second, and optional third
20 and fourth, electrochemical reactions occurs may be the formal potential of each of the first and second electrochemical reactions. The formal potential may be measured using any suitable technique. In a preferred embodiment, the first and second, and optional third and fourth potentials are measured by a pulse voltammetry method, including, but not limited to, sampled current polarography, differential pulse voltammetry, normal pulse
25 voltammetry, and square wave voltammetry.

The first potential at which the first electrochemical reaction occurs may be determined by, for example, a voltammetry method, e.g. a pulse voltammetry method such as a square wave voltammetry method, in which a peak in current is seen at the first potential.

30 Likewise, the second potential at which the second electrochemical reaction occurs may be determined by, for example, a voltammetry method, e.g. a pulse voltammetry method such as a square wave voltammetry method, in which a peak in current is seen at the second potential.

35

Likewise, the third potential at which the third electrochemical reaction occurs may be determined by, for example, a voltammetry method, e.g. a pulse voltammetry method such as a square wave voltammetry method, in which a peak in current is seen at the third potential.

5

Likewise, the fourth potential at which the fourth electrochemical reaction occurs may be determined by, for example, a voltammetry method, e.g. a pulse voltammetry method such as a square wave voltammetry method, in which a peak in current is seen at the fourth potential.

10

In an embodiment, the conditions for carrying out the square wave voltammetry use a frequency of from 0.1 to 100 Hz, optionally from 10 to 80 Hz, optionally from 40 to 60 Hz, optionally about 50 Hz; and/or a step potential of from 0.01 to 1 mV, optionally from 0.05 to 0.2 mV, optionally about 0.1 mV; and/or an amplitude of from 1 to 50 mV, optionally from 10 to 40 mV, optionally from 20 to 30 mV, optionally about 25 mV.

15

The method involves converting the difference between the first and second potentials to a value of humidity. This converting may be carried out by using a predetermined relationship between the difference between the first and second potentials and known humidities, which may have been determined by a calibration step.

20

In some circumstances, the relationship between humidity and the difference between first and second potentials may be adequately described by a linear equation. Accordingly, the difference ($E_{1/2}$) between the first and second potentials can be represented by the Formula (a)

25

$$E_{1/2} = C + nRH$$

Formula (a)

where C is a constant and n is a coefficient, and RH is humidity, and $E_{1/2} = E_2 - E_1$, where E_1 is the first potential and E_2 is the second potential. With this relationship, for a system of interest, e.g. the humidity sensor and/or electrochemical sensor described herein, a calibration can be carried out for the first and second electrochemical reactions to determine values for $E_{1/2}$ over a range of known humidities to determine C and n. Accordingly, once C and n are known for a system, e.g. the humidity sensor and/or

30

electrochemical sensor described herein, if $E_{1/2}$ is determined at an (unknown) humidity of interest, an RH value can be determined for the humidity of interest.

In an alternative embodiment, if desired, higher order polynomials may be used for the relationship between the difference between the first and second potentials and humidity. This may be used to obtain a higher degree of accuracy when measuring humidity. For example, the relationship may be expressed by a second degree polynomial of Formula (b)

$$E_{1/2} = C + nRH + o(RH)^2 \quad \text{Formula (b)}$$

wherein $E_{1/2}$, C, n and RH are as defined above for formula (a) and o is a further coefficient. Again, for a system of interest, C, n and o may be determined in a calibration step by measuring $E_{1/2}$ over a range of known humidities. Higher degree polynomials relating $E_{1/2}$ and RH can also be used, such as third degree polynomials, fourth degree polynomials, and so on.

The converting may be carried out automatically using an appropriate calculation medium, which may be a computer program. The computer program may be stored/distributed on a suitable medium, such as an optical storage medium or a solid-state medium supplied together with or as part of the humidity sensor and/or electrochemical sensor, but may also be distributed in other forms, such as via the Internet or other wired or wireless telecommunication systems.

In an alternative embodiment, the difference in the first and second potentials can be compared against a database containing calibrated values for differences between first and second potentials at a range of known humidities, to give a value in the humidity of interest.

In an embodiment, the method involves a calibration step to determine a relationship between known humidities and the difference in the potential between the potentials at which first and second reactions occur, and this relationship is used to convert the difference between the first and second potentials determined in the method to the value of humidity.

The calibration step may be an automatic calibration step carried out by the humidity sensor and/or electrochemical sensor.

The difference between the first and second potentials (e.g. at the humidity of interest or at 25 °C), is preferably at least 0.1 V, preferably at least 0.2 V, preferably at least 0.3 V, preferably at least 0.4 V, preferably at least 0.5 V, preferably at least 0.6 V, preferably at least 0.7 V, preferably at least 0.8 V, preferably at least 0.9 V, preferably at least 1 V. It has been found that the greater the difference between the first and second potentials, the greater the accuracy in the measurement of humidity using this difference. The first and second species being reduced in the first and second electrochemical reactions can be appropriately selected to increase the difference in potentials as desired.

The method optionally additionally involves converting the difference between the third and fourth potentials to a value of temperature. This converting may be carried out by using a predetermined relationship between the difference between the third and fourth potentials and known temperatures, which may have been determined by a calibration step. The present inventors have found that the difference between the third and fourth potentials typically varies linearly with temperature, and that there is a high correlation between the two. Typically, the present inventors have found that the difference ($E_{4/3}$) between the third and fourth potentials can be represented by the Formula (c)

$$E_{4/3} = C_T + pT \quad \text{Formula (c)}$$

where C_T is a constant and p is a coefficient, and T is temperature, and $E_{4/3} = E_4 - E_3$, where E_3 is the third potential and E_4 is the fourth potential. With this relationship, for a system of interest, e.g. the humidity sensor and/or electrochemical sensor described herein, a calibration can be carried out for the third and fourth electrochemical reactions to determine values for $E_{4/3}$ over a range of known temperatures to determine C_T and p . Accordingly, once C_T and p are known for a system, e.g. the humidity (and temperature) sensor and/or electrochemical sensor described herein, if $E_{4/3}$ is determined at an (unknown) temperature of interest, a value T can be determined for the temperature of interest. In an alternative embodiment, if desired, higher order polynomials may be used for the relationship between the difference between the third and fourth potentials and temperature. For example, the relationship may be expressed by a second degree polynomial of formula (d)

$$E_{4/3} = C_T + pT + qT^2$$

Formula (d)

wherein $E_{4/3}$, C_T , p and T are as defined above for formula (c) and q is a further coefficient.

5 Again, for a system of interest, C_T , p and q may be determined in a calibration step by measuring $E_{4/3}$ over a range of known temperatures. Higher degree polynomials relating $E_{4/3}$ and T can also be used, such as third degree polynomials, fourth degree polynomials, and so on. However, in many circumstances, the relationship between $E_{4/3}$ and T has been found to be sufficiently linear that formula (c) can be used and is adequate for
10 temperature measurement.

The converting may be carried out automatically using an appropriate calculation medium, which may be a computer program. The computer program may be stored/distributed on a suitable medium, such as an optical storage medium or a solid-state medium supplied
15 together with or as part of the humidity sensor and/or electrochemical sensor, but may also be distributed in other forms, such as via the Internet or other wired or wireless telecommunication systems.

In an alternative embodiment, the difference in the third and fourth potentials can be
20 compared against a database containing calibrated values for differences between third and fourth potentials at a range of known temperatures, to give a value in the temperature of interest.

In an embodiment, the method involves a calibration step to determine a relationship
25 between known temperatures and the difference in the potential between the potentials at which third and fourth reactions occur, and this relationship is used to convert the difference between the third and fourth potentials determined in the method to the value of temperature.

30 The calibration step may be an automatic calibration step carried out by the humidity (and temperature) sensor and/or electrochemical sensor.

The difference between the third and fourth potentials (e.g. at the temperature of interest or at 25 °C), is preferably at least 0.1 V, preferably at least 0.2 V, preferably at least 0.3 V,
35 preferably at least 0.4 V, preferably at least 0.5 V, preferably at least 0.6 V, preferably at

least 0.7 V, preferably at least 0.8 V, preferably at least 0.9 V, preferably at least 1 V. It has been found that the greater the difference between the third and fourth potentials, the greater the accuracy in the measurement of temperature using this difference. The third and fourth species being reduced in the third and fourth electrochemical reactions can be appropriately selected to increase the difference in potentials as desired.

The method may be carried out at any suitable temperature. In some examples, the method is carried out at a temperature of 0 °C or above, optionally in the temperature range of from 0 °C to 500 °C, optionally from 0 °C to 300 °C, optionally from 0 °C to 200 °C, optionally from 0 °C to 100 °C, optionally from 0 °C to 50 °C.

The first and second electrochemical reactions, and optional third and fourth electrochemical reactions, may be carried out in any suitable carrier medium, preferably an electrolyte. The first and second, and optional third and fourth, species that undergo the first and second, and optional third and fourth, electrochemical reactions may be dissolved or suspended in the carrier medium and/or immobilised on the surface of a working electrode, which may be in contact with a carrier medium. The carrier medium may be a protic or non-protic solvent. Such a carrier medium may comprise a solvent. The solvent may be a polar or a non-polar solvent, dependent on the nature of the first and second species undergoing the first and second electrochemical reactions. The solvent may be a non-polar, non-protic solvent. In some examples the solvent may be selected from xylene, methylene chloride, perchloroethylene, chloroform, carbon tetrachloride, chlorobenzene, acetone, 2-butanone, 2-pentanone, methyl acetate, ethyl acetate, propyl acetate, butyl acetate, methyl propionate, ethyl propionate, a dialkylether of ethylene glycol wherein the alkyl groups contain 1 to 4 carbon atoms, a dialkylether of propylene glycol wherein the alkyl groups contain 1 to 4 carbon atoms, paraffinic solvents such as naphtha, hexane, benzene, toluene, diethyl ether, chloroform, and mixtures thereof. The solvent may comprise a protic solvent selected from water, alcohols, e.g. alkanols such as ethanol, and carboxylic acids.

The carrier medium may comprise a solid electrolyte. The solid electrolyte may comprise a protonic conductive electrolyte polymer. The solid electrolyte may be selected from a perfluorinated ion-exchange polymer, e.g. such as that available as Nafion, or a conductive polymer selected from poly(ethylene glycol), poly(ethylene oxide), poly(propylene carbonate).

In an embodiment, the first and second (and optionally third and fourth) reactions are carried out in an ionic liquid. Generally, ionic liquids are non-aqueous, organic salts comprising ions where the positive ion is charge-balanced with a negative ion. Ionic liquids have low melting points, often below 100°C, undetectable or very low vapour pressure, and good chemical and thermal stability. The cationic charge of the salt is localized over hetero atoms, such as nitrogen, phosphorous, sulphur, arsenic, boron, antimony, and aluminium, and the anions may be any inorganic, organic, or organometallic species. The ionic liquid may be selected from, but is not limited to, imidazolium ionic liquids, pyridinium ionic liquids, tetra alkyl ammonium ionic liquids, and phosphonium ionic liquids. Imidazolium, pyridinium, and ammonium ionic liquids have a cation comprising at least one nitrogen atom. Phosphonium ionic liquids have a cation comprising at least one phosphorus atom. The ionic liquid may comprise a cation selected from alkyl imidazolium, di-alkyl imidazolium, and combinations thereof. In an embodiment, each of the alkyl groups independently contain from one to ten carbon atoms. Dialkyl imidazolium ionic liquids have a cation comprising two alkyl groups extending from a five membered ring of three carbon and two nitrogen atoms, most commonly from the two nitrogen atoms of this five membered ring; the two alkyl groups may each independently be selected from C1 to C10 alkyl groups, optionally from C1 to C6 alkyl groups, optionally from methyl, ethyl, propyl, butyl, pentyl and hexyl. In an embodiment, the dialkyl imidazolium ionic liquids have a 1-alkyl-3-methyl-imidazolium cation, wherein alkyl may be selected from C1 to C10 alkyl groups, optionally from C1 to C6 alkyl groups, optionally from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl and decyl. The ionic liquid cation may be selected from 1-methyl-3-methylimidazolium, 1-ethyl-3-methylimidazolium, 1-propyl-3-methylimidazolium, 1-butyl-3-methyl imidazolium, 1-pentyl-3-methyl imidazolium, 1-hexyl-3-methyl imidazolium, and combinations thereof.

In an embodiment, the ionic liquid may have an N-alkyl-pyridinium cation, wherein the alkyl is selected from C1 to C10 alkyl groups, optionally from C1 to C6 alkyl groups, optionally methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl and decyl.

In an embodiment, the ionic liquid may have a tetraalkyl ammonium cation, wherein the alkyl is selected from C1 to C10 alkyl groups, optionally from C1 to C6 alkyl groups, optionally methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl and decyl.

In an embodiment, the ionic liquid may have a tetraalkyl phosphonium cation, wherein the alkyl is selected from C1 to C10 alkyl groups, optionally from C1 to C6 alkyl groups, optionally methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl and decyl.

- 5 In an embodiment, the ionic liquid comprises an anion selected from a borate (including, but not limited to, tetracyanoborate and tetrafluoroborate), PF_6 , bistrifluoromethylsulfonylimide, halides, acetate, CF_3CO_2^- , CF_3SO_2^- , carboxylates, NO_3^- and combinations thereof.
- 10 In an embodiment, the ionic liquid is a room temperature ionic liquid, i.e. it is liquid at 25°C .

- Optionally, the carrier medium, e.g. an ionic liquid, is within a solid support medium, preferably within the pores of a porous solid support medium. The solid support medium
- 15 may comprise a mesoporous material, which may be a material having pores with a diameter in the range of from 1 to 75 nm, more particularly in the range of from 2 to 50 nm. The solid support medium may comprise a mesoporous material selected from zeolites, clays, and metal oxides, including, but not limited to, titanium oxide (TiO_2), aluminium oxide (Al_2O_3), zirconium oxide (zirconia, Zr_2O_4), and silicon oxide (silica, SiO_2),
- 20 or mixtures thereof, such as silica-alumina.

- Preferably, the viscosity of the ionic liquid varies with a change in atmospheric humidity. The present inventors have found that the higher the change in viscosity with the change in humidity, the greater the variance of the difference between the first and second
- 25 potentials with a change in humidity, and more sensitive the method and sensors described herein can be. The present inventors have found that using high viscosity ionic liquids seems to promote a high variance of the difference between first and second potentials with changes in humidity.

- 30 Optionally, the ionic liquid has a dynamic viscosity, as measured at 20°C , of at least 50 cP. Optionally, the ionic liquid has a dynamic viscosity, as measured at 20°C , of at least 100 cP. Optionally, the ionic liquid has a dynamic viscosity, as measured at 20°C , of at least 150 cP. Dynamic viscosity can be measured using known techniques in the field, for example by using a viscometer or rheometer. An example of a commercially available
- 35 viscometer is an Anton Paar SVM 3000 Stabinger Viscometer. The viscosity may be

measured at standard pressure (e.g. 101.325 kPa). The viscosity measured may be that of the ionic liquid in pure form, i.e. absent any of the other components (e.g. reaction species) that may be present in the electrochemical reactions carried out.

- 5 Optionally, the ionic liquid comprises a perfluorinated alkyl fluorophosphate anion. These can be very viscous ionic liquids, and seem to display a high variation in viscosity with changes in humidity. The associated cation may be any mentioned herein.

- Optionally, the ionic liquid comprises a tris(pentafluoroethyl)trifluorophosphate anion.
- 10 Ionic liquids containing this anion are available commercially, for example from Merck. The associated cation may be any mentioned herein. In some examples, the ionic liquid is selected from 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate, 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate, 1-(2-methoxyethyl)-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate and N-ethyl-N,N-dimethyl-(2-
- 15 methoxyethyl)ammonium tris(pentafluoroethyl)trifluorophosphate.

- Optionally, the method also involves measuring temperature in accordance with the second aspect, and the third and fourth reactions are carried out in the same carrier medium, e.g. ionic liquid, as the first and second reactions.

20

If the first and second, and optional third and fourth reactions are carried out in a carrier medium, the method may involve allowing the humidity in any gas in contact with the carrier medium to equilibrate with the water content in the carrier medium, to allow for improved accuracy in the measurement.

25

- The method may further involve obtaining further electrochemical information at the humidity (and optionally temperature) of interest. For example, the method may further involve obtaining electrochemical information about a species, e.g. a species other than those involved in, e.g. oxidised or reduced in, the first and/or second, and optional third
- 30 and/or fourth reactions. A species other than those involved in, e.g. oxidised or reduced in, the first and/or second, and optional third and/or fourth, reactions may be termed a further species or a species to be sensed herein. The method may further involve determining the concentration of a species, which may be the same as or different from, the species involved in the first and second, and optional third and fourth reactions,
- 35 wherein the concentration is determined by electrochemical data; the determining of the

concentration of the species may be carried out before, during or after determining the first and second, and optional third and fourth, potentials. The determining of the first and second, and optional third and fourth, potentials may be carried out using a working electrode and a counter electrode in a voltammetry technique, and the working and counter electrodes are also used to obtain further electrochemical information at the humidity (and optionally temperature) of interest.

The determining of the first and second, and optional third and fourth, potentials may be carried out using a working electrode and a counter electrode in a voltammetry technique, wherein the first electrochemical reaction involves oxidation or reduction of a first species and the second electrochemical reaction involves oxidation or reduction of a second species (and optionally the third and fourth electrochemical reaction involves oxidation or reduction of a third and fourth chemical species) respectively, wherein first and second (and optionally third and fourth) species are in a carrier medium and/or immobilised on a surface of the working electrode in contact with the carrier medium, and the working and counter electrodes are also used to obtain further electrochemical information at the humidity (and optionally temperature) of interest, including, but not limited to the concentration of a species in the carrier medium, e.g. a species other than any or all of the first, second, third and fourth species in the carrier medium.

In an embodiment, the method may be carried out in or the humidity sensor may be or comprise an electrochemical sensing device, e.g. an electrochemical gas sensing device. Electrochemical sensing devices are known to the skilled person. An electrochemical sensing device may be termed an electrochemical sensor. An electrochemical sensing device typically comprises a working electrode, a counter electrode and an electrolyte in contact with the working electrode and the counter electrode. The working electrode is sometimes termed a sensing electrode. The working and counter electrodes may be disposed opposite one another or the working and counter electrodes may be disposed on the same face of a substrate and spaced apart from one another. The electrochemical sensing device may further comprise a reference electrode. The working electrode, counter electrode, the electrolyte, and, if present, the counter electrode are typically in a housing. For electrochemical gas sensors, the housing typically comprises a means for controlling access of the gas to a counter electrode. The means for controlling access of the gas to the counter electrode may be a gas phase diffusion barrier, a Knudsen barrier or a solid membrane. Typically, in operation, a potential is applied between the working

electrode and counter electrode, with the potential being varied as required, and the current monitored. The presence and concentration of the species to be sensed, e.g. a gas, within the electrolyte can be monitored using known relationships between the concentration of the species to be sensed, the potential applied between the working electrode and the counter electrode and the resulting current.

Electrochemical sensors are described, for example, in US 5,668,302, EP0604012, US 5,746,899, US 5,746,899, WO 2007/100691, WO2005/017516, WO2008/110830, and WO 2008/057777, each of which is incorporated herein by reference in its entirety.

In an embodiment, the method is carried out in an electrochemical sensing device comprising a working electrode and a counter electrode, wherein the working electrode and counter electrode are used to determine the first potential at which the first electrochemical reaction occurs and the second potential at which the second electrochemical reaction occurs (and optionally the third and fourth potentials at which the third and fourth reactions occur respectively). The working and counter electrodes may also be used to obtain electrochemical information, about the species to be sensed, e.g. a gas, which may be used to determine the presence of and/or concentration of the species to be sensed within the sensor and/or in the ambient environment around the sensor; this may be before, during or after the first and second, and optional third and fourth, potentials have been determined. The species to be sensed may be detected by measuring a potential at which this species is oxidised or reduced; and the oxidation or reduction of this species may constitute one of the first and second (and, if carried out, third and fourth) electrochemical reactions.

The further species or the species to be sensed may be selected from glucose, NH_3 , AsH_3 , halogens (such as F_2 , Cl_2 , Br_2 and I_2), CO , CO_2 , ClO_2 , B_2H_6 , GeH_4 , H_2 , HCl , HCN , HF , O_2 , O_3 , H_2S , nitrogen oxides (such as NO and NO_2), PH_3 , SiH_4 and sulphur oxides (such as SO_2).

As described herein, the present invention provides a humidity sensor, wherein the sensor is adapted to:

determine, at a humidity of interest, a first potential at which a first electrochemical reaction occurs;

determine, at the humidity of interest, a second potential at which a second electrochemical reaction occurs;

determine the difference between the first and second potentials;

convert the difference between the first and second potentials to a value of humidity.

5

Optionally, the humidity sensor is also a temperature sensor, wherein the sensor is further adapted to:

determine, at a temperature of interest, a third potential at which a third electrochemical reaction occurs;

10 determine, at the temperature of interest, a fourth potential at which a fourth electrochemical reaction occurs;

determine the difference between the third and fourth potentials;

convert the difference between the third and fourth potentials to a value of temperature.

15

Preferably, the humidity sensor is further adapted to carrying out any of the optional or preferred features of the method described herein.

The humidity sensor may be an electrochemical sensor as described herein.

20

The present invention further provides an electrochemical sensor for sensing a species, the sensor comprising:

a working electrode, a counter electrode and a carrier medium in contact with the working electrode and the counter electrode, wherein the carrier medium contains, and/or

25 the working electrode has immobilised on a surface thereof, a ferrocene compound containing a single iron atom and a multiferrocene compound, and the carrier medium is an ionic liquid having a dynamic viscosity, as measured at 20 °C, of at least 50 cP. The sensor may be adapted to carrying out the method described herein. The ferrocene compound containing a single iron atom may be for carrying out, and may be the first and
30 third species in, the first, and optional third reactions. The multiferrocene compound may be for carrying out the second and optional fourth reactions, and may be, in different oxidation states, the second and fourth species. The ferrocene compound containing a single iron atom and the multiferrocene compound may be as described herein.

The ionic liquid may be as described above for the method. In some examples, the ionic liquid has a dynamic viscosity, as measured at 20 °C, of at least 100 cP. In some examples, the ionic liquid comprises a perfluorinated alkyl fluorophosphate anion.

- 5 Preferably, the humidity sensor is also an electrochemical sensor for sensing and/or determining the concentration of a species within the sensor, e.g. a species other than a species involved in the first and/or second, and optional third and/or fourth reactions.

10 The humidity sensor may comprise working and counter electrodes, and an electrolyte in contact with the sensors, wherein, in use, the working and counter electrodes are used to determine the first and second (optionally third and fourth) potentials and obtain electrochemical information for sensing and/or determining the concentration of a species within the sensor other than a species involved in the first and second (and optional third and fourth) reactions. The electrolyte may be as described herein. The electrolyte may
15 comprise an ionic liquid, which may be as described herein.

The electrolyte must comprise at least two different chemical entities, which, in use, are either oxidised or reduced in the first and second, and optional third and fourth electrochemical reactions, and the oxidation or reduction of the two different chemical
20 entities occur at different potentials from each other.

The first and third electrochemical reactions may be the same reaction.

25 The humidity sensor and/or electrochemical sensor may also be or comprise a gas sensor. The gas sensor may be adapted to sense the presence and/or concentration of a gas selected from NH₃, AsH₃, halogens (such as F₂, Cl₂, Br₂ and I₂), CO, CO₂, ClO₂, B₂H₆, GeH₄, H₂, HCl, HCN, HF, O₂, O₃, H₂S, nitrogen oxides (such as NO and NO₂), PH₃, SiH₄ and sulphur oxides (such as SO₂).

30 The humidity sensor and/or electrochemical sensor may be a pH sensor.

The humidity sensor and/or electrochemical sensor may also be or comprise an electrochemical biosensor. The electrochemical biosensor may be for detecting one or more species of biological interest. The electrochemical biosensor may have a working
35 electrode having probe molecules immobilised thereon for binding to a target. The probe

molecules may be selected from, but are not limited to, one or more of a peptide, a peptide aptamer, a DNA aptamer, a RNA aptamer, and an antibody. The probe molecules may be selective for a target selected from, but not limited to, proteins, polypeptides, antibodies, nanoparticles, drugs, toxins, harmful gases, hazardous chemicals, explosives, viral particles, cells, multi-cellular organisms, cytokines and chemokines, ganietocyte, organelles, lipids, nucleic acid sequences, oligosaccharides, chemical intermediates of metabolic pathways and macromolecules.

The electrochemical sensor may be calibrated to take into account the value in humidity (and optionally temperature) obtained by the humidity sensor when calculating the concentration of a species being sensed in the electrochemical sensor.

The invention further provides an electrochemical sensor for sensing a species, the sensor comprising

a working electrode, a counter electrode and a carrier medium in contact with the working electrode and the counter electrode, wherein the carrier medium contains, and/or the working electrode has immobilised on a surface thereof, one or more species, other than the species to be sensed, that is or are capable of undergoing a first electrochemical reaction at a first potential, and a second electrochemical reaction at a second potential.

The working electrode, counter electrode and carrier medium, which may be an electrolyte, may be as described herein. The one or more species may comprise a ferrocene compound. The electrochemical sensor is preferably adapted to carrying out the method of the first aspect as described herein.

Optionally, the carrier medium contains, and/or the working electrode has immobilised on a surface thereof, one or more additional species which are capable of undergoing a third electrochemical reaction at a third potential and a fourth electrochemical reaction at a fourth potential. The first and third electrochemical reactions can be the same reaction.

The one or more species may comprise one or more of first, second, third or fourth species described above.

In an embodiment, the carrier medium comprises an ionic liquid. The electrochemical sensor may also be an humidity sensor, as described herein, e.g. adapted to

determine, at a humidity of interest, a first potential at which a first electrochemical reaction occurs;

determine, at the humidity of interest, a second potential at which a second electrochemical reaction occurs;

5 determine the difference between the first and second potentials;

convert the difference between the first and second potentials to a value of humidity.

Optionally, the electrochemical sensor is additionally adapted to:

10 determine, at a temperature of interest, a third potential at which a third electrochemical reaction occurs;

determine, at the temperature of interest, a fourth potential at which a fourth electrochemical reaction occurs;

determine the difference between the third and fourth potentials;

15 convert the difference between the third and fourth potentials to a value of temperature.

The electrochemical sensor and/or humidity sensor may comprise a separable device that can control the electrochemical sensor and/or temperature sensor such that it carries out and/or controls the method described herein; the separable device may carry out the
20 converting step as described herein. The electrochemical sensor and/or humidity sensor and/or separable device may contain an appropriate computer program for controlling the electrochemical sensor and/or humidity sensor and/or separable device, such that the method as described herein is carried out. The computer program may be on suitable hardware, firmware or other storage medium that may form part of the electrochemical
25 sensor and/or humidity sensor and/or the separable device.

The electrodes described herein, e.g. for use in the method, humidity sensor and/or the electrochemical sensor, may be any suitable electrodes. Typically, a working and a counter electrode are used, and, optionally a reference electrode may be used in the
30 determining of the potential of the first and second reactions (and optionally the third or fourth reactions) and/or in the electrochemical sensing.

The shape and configuration of the electrodes is not particularly restricted. The electrodes may be in the form of points, lines, rings and flat planar surfaces. In an embodiment, the
35 working electrode and the counter electrode are disposed opposite one another within a

housing. In an alternative embodiment, the working and reference electrodes are disposed on the same face of a substrate. In an embodiment, the electrodes are disposed on the same face of the substrate and form an interlocking pattern.

- 5 The working and counter electrodes may have any appropriate size, e.g. a maximum distance across their face of from 1 to 1000 microns, optionally from 1 to 500 microns, optionally from 1 to 50 microns. The gap between the working and counter electrodes may be from 20 and 1000 microns, optionally from 50 to 500 microns.
- 10 The counter electrode and working electrode are optionally of equal size. Preferably, the surface area of the counter electrode is greater than that of the working electrode.

- In the method, in the humidity sensor, and/or electrochemical sensor, the electrodes may each be supported on a substrate, which may form part of a housing optionally enclosing
- 15 the electrodes and any carrier medium or electrolyte that is in contact with the electrodes. The substrate and/or housing may comprise any inert, non-conducting material, which may be selected from, but is not limited to, ceramic, plastic and glass.

- The working, counter and, if present, reference electrodes each comprise any suitable
- 20 electrically conducting material, e.g. a metal, an alloy of metals and/or carbon. The working, counter and, if present, reference electrodes may comprise a transition metal, for example a transition metal selected from any of groups 9 to 11 of the Periodic Table. The working, counter and, if present, reference electrode may each independently comprise a metal selected from, but not limited to, rhenium, iridium, palladium, platinum,
- 25 copper, indium, rubidium, silver and gold.

Embodiments of the present invention will now be described with reference to the following non-limiting Examples and the accompanying drawings.

Examples

The present inventors describe below the simultaneous measurement of temperature and humidity by analysing square wave voltammetric responses of two ferrocene derivatives, decamethylferrocene (DmFc) and 1,2-diferrocenylethylene (bisferrocene, BisFc) in 1-(2-methoxyethyl)-1-methyl-pyrrolidinium tris(pentafluoroethyl)trifluorophosphate ([Moepyrr][FAP]). These two molecules produce three peaks in square wave voltammetry. Through study of the peak potentials of BisFc/BisFc⁺ (vs. DmFc/DmFc⁺) and BisFc⁺/BisFc²⁺ (vs. DmFc/DmFc⁺) over a temperature range of 298K to 318K and humidity range of 1% to 50% using square wave voltammetry, the temperature and humidity dependences of the relative peak potentials were investigated. A reliable method to calculate the humidity and temperature based on the voltammetric experiment is characterised and demonstrated.

The present inventors propose a method to directly detect temperature and humidity at the electrode solution interface, providing electrochemical temperature and humidity sensing in their own right or, if desired, a sensing approach for immediate integration with other voltammetric sensing. This proposed sensor is voltammetrically based and measures the temperature and humidity via formal potentials. The formal potential dependence on temperature is related to the entropy change of the redox process in an electrochemical reaction,⁸ and a temperature sensor has been developed according to this principle.⁹ Building on the present inventors' success in monitoring temperature using differences in formal potentials of two redox couples, they have now developed this method to simultaneously measure the two quantities, temperature and humidity. This requires two independent formal potential measurements to be made. Furthermore, to simplify ease of measurement, efforts are made to select species such that the temperature dependent pair is humidity independent and vice versa.

1-(2-Methoxyethyl)-1-methyl-pyrrolidinium tris(pentafluoroethyl)trifluorophosphate, is a very high viscous RTIL, and its conductivity and viscosity change dramatically with the humidity.¹⁰ This is utilised in the work described below.

In the Examples, the following chemicals were used:

Ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$, Aldrich, 98%), decamethylferrocene ($\text{Fe}(\text{C}_{10}\text{H}_{15})_2$, Fluka, 95%), acetonitrile (MeCN, Fischer Scientific, dried and distilled, 99%), tetra-*n*-butylammonium perchlorate (TBAP, Fluka, Puriss electrochemical grade, 99%), 1-Ethyl-3-methylimidazolium tetracyanoborate ([Emim][TCB], high purity, kindly donated by Merck) and 1-propyl-3-methylimidazolium bistrifluoromethylsulfonylimide ([Pmim][NTf₂], prepared in house from the corresponding bromide salt)¹⁵ and 1-(2-methoxyethyl)-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate ([Moepyrr][FAP], kindly donated by Merck) were used as received without further purification. 1,2-Diferrocenylethylene (Bisferrocene, BF) was synthesised using the following method: TiCl_4 (0.39 mL, 3.50 mmol) was added dropwise to anhydrous THF (10 mL) at 0 °C under N_2 . A solution of ferrocenecarboxaldehyde (500 mg, 2.34 mmol) in anhydrous THF (5 mL) and Zn powder (300 mg, 4.59 mmol) were sequentially added to the yellow solution at 0 °C. The resultant black suspension was heated at reflux for four hours. After cooling, the mixture was poured onto ice water (50 mL), and sat. aq. NaHCO_3 (30 mL) was added. The resultant mixture was extracted with CH_2Cl_2 (3 × 30 mL). The organics were dried over MgSO_4 and concentrated *in vacuo* to give the title compound (340 mg, 73%) as a dark orange solid; δ_{H} (400 MHz, CDCl_3) 4.18 (10H, s, Cp), 4.33 (4H, s, Cp), 4.55 (4H, s, Cp), 6.18 (2H, s, CH=CH).

In the Examples, the following instruments were used:

All electrochemical experiments were performed using a computer-controlled PGSTAT30-Autolab potentiostat (Eco-Chemie, Netherlands). For experiments in acetonitrile, solutions were housed in a sealed glass vial, with a three-electrode arrangement consisting of a 5.05 μm diameter Pt working electrode, a silver wire reference electrode and Pt coil wire counter electrode. The platinum microdisk working electrodes were polished on soft lapping pads (Kemet Ltd., UK) using alumina powders (Buehler, IL) of sizes 1.0, 0.3 mm and 0.05 mm. The electrode diameters were calibrated electrochemically by analysing the steady-state voltammetry of a 2mM solution of ferrocene in MeCN containing 0.1 M TBAP, using a diffusion coefficient for ferrocene of $2.30 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at 298 K.¹⁶ The experiments involving ionic liquids were studied using a three-electrode arrangement, consisting of a 5.05 μm radius platinum working electrode and two 0.5 mm diameter silver wires acted as *quasi*-reference and counter electrodes. The microelectrode was modified with a small section of disposable pipette tip to form a cavity on the electrode surface into which microlitre quantities of RTIL were added. The electrodes were housed in a T-cell (reported previously)¹⁷, specifically designed to allow samples to be studied under a controlled

atmosphere. Prior to the addition of humidified air, the whole system was degassed under vacuum for at least two hours to remove water and other impurities.^{11, 18, 19} The humidified air was realised via the following method: the inlet line of the gas is divided into two lines, with one connected to a drying column and another to a Dreschel bottle which is filled with deionised water. These two lines then emerge into a common outlet line, which allows the gas to flow into the T-cell. The humidity is controlled by the flow meters in the dry and wet line respectively. The drying column consists of concentrated silica and solid calcium chloride. Before the electrochemical measurements, gas was run for at least 15 hours to ensure equilibrium was established. For experiments excluding gases, the ionic liquid was constantly purged under vacuum during experimental analysis.

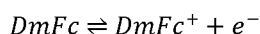
In the Examples, the values of humidity were recorded using an ADC-16 pico-logger (Honeywell, UK). The humidity is described using the relative humidity equation below,²⁰

$$RH (\%) = \frac{e_w}{e_w^*} \times 100$$

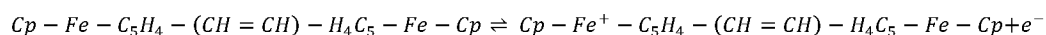
where e_w is the partial pressure of water vapour (H_2O) in the mixture and e_w^* is the saturated vapor pressure of water at a prescribed temperature. The variation of humidity during an experiment was no more than 1% RH. All experiments were performed inside a thermostatted box (previously described by Evans et al.)²¹ which also functioned as a Faraday cage. All experiments were repeated at least three times and the variation of all results (i.e. peak potential) for the same experiment was less than 3 mV which was calculated using standard deviations from at least three sets of experiments under the same experimental conditions.

In these Examples, the following oxidative redox reactions in different ionic liquids were investigated,

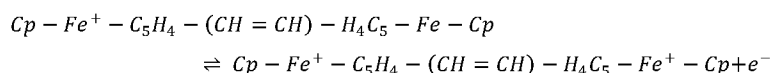
Reaction 1:



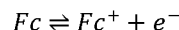
Reaction 2:



Reaction 3:



Reaction 4:



where Fc is ferrocene, DmFc is decamethylferrocene and each redox reaction is associated with a formal potential $E_{f,1}^o$, $E_{f,2}^o$, $E_{f,3}^o$ and $E_{f,4}^o$ respectively. See also Figure 8 for chemical structures.

5

The following differences in formal potential are investigated adopting the notations given,

$$\Delta E_{1/2} = E_{f,2}^o - E_{f,1}^o$$

$$\Delta E_{1/3} = E_{f,3}^o - E_{f,1}^o$$

$$\Delta E_{2/3} = E_{f,3}^o - E_{f,2}^o$$

$$\Delta E_{1/4} = E_{f,4}^o - E_{f,1}^o$$

10 In the Examples, the peak potential difference of two redox centres is measured to avoid the need for a perfectly stable reference electrode⁹ and hence the choice of redox probes is important. Decamethylferrocene shows many interesting electrochemical properties as compared to other ferrocene derivatives, one of which as being relative insensitive to solute composition makes it a very useful redox standard,²² especially in the present humidity study. On the other hand, previous work indicates that the first and second
15 oxidation potential of bisferrocene can be tuned by varying the anion component of ionic liquid.¹⁰ As the change in humidity alters the composition of ionic liquid the peak potential differences of bisferrocene and decamethylferrocene may allow us to measure the humidity of air. These systems were accordingly investigated in 1-(2-methoxyethyl)-1-methyl-pyrrolidinium tris(penta-fluoroethyl)trifluorophosphate ([Moepyrr][FAP], see Figure
20 9) not only due to its very low melting point (223 K), high decomposition temperature (523 K) and negligible volatility which ensure that this system works over a large temperature and pressure range, but also because this ionic liquid is highly viscous and any additional water may dramatically change its physical properties and hence associated formal.^{23, 24}

The volatility of decamethylferrocene and bisferrocene in [Moepyrr][FAP] under vacuum was tested using steady state voltammetry where only a slight reduction in the concentration was seen (no more than 5%) in steady state current over a period of 20 hours. This shows that both decamethylferrocene and bisferrocene have a negligible volatility in the RTIL, in contrast to ferrocene.^{25, 26}

1mM decamethylferrocene and 1mM bisferrocene in [Moepyrr][FAP] were then examined at different temperatures (in the range of 298 K to 318 K) under vacuum using square wave voltammetry at a potential range of -0.1 V to 1.0 V vs. Ag, where the redox reactions correspond to Reactions 1 to 3. The formal potentials of redox couples were readily evaluated using square wave voltammetry (SWV) as this records the current difference in the oxidative and reductive direction as a function of staircase potential.²⁷⁻²⁹ The peak potential in the square wave voltammetry is close to the formal potential of the redox couple studied.³⁰ The experimental conditions for SWV were optimised for maximum current using a frequency of 50 Hz, a step potential of 0.1 mV and amplitude of 25 mV.

Example 1

Figure 1a shows the square wave voltammetric responses for the oxidation of 1.0 mM decamethylferrocene and 1.0 mM bisferrocene in [Moepyrr][FAP] over a temperature range of 298-318 K. The increase in the peak current with temperature is due to the fact that the diffusion is faster at higher temperature owing to the reduced solvent viscosity. The peaks in Figure 1 from negative to positive potential (marked with peaks 1, 2 and 3) are due to the Reactions 1 to 3, respectively. The plots of $\Delta E_{1/3}$, $\Delta E_{2/3}$ and $\Delta E_{1/2}$ against temperature are depicted in Figure 1b. It can be seen from these plots that the peak differences remain almost unchanged with the varying temperatures. This 'thermal insensitive' observation reflects that for a fast electron transfer reversible process, the temperature dependence of these two formal potentials is related to the entropy change associated with the electrochemical process via,

$$F \frac{\partial E_f^o}{\partial T} = \Delta S^o \quad \text{Equation 1}$$

where E_f^o is the formal potential, T is the temperature, S is the entropy and F is the Faraday constant. The peak potential difference varies with temperature only if the temperature dependence of the two formal potentials of two redox centres is different.

5

Example 2

There are basic structural similarities between decamethylferrocenium and the singly charged bisferrocenium (where the charge is located in one redox center of the bisferrocenium), as well as their unoxidised forms, which leads to the observed temperature independent peak difference ($\Delta E_{1/2}$). This is consistent with the observations in the square wave voltammetry for the oxidation of decamethylferrocene (Reaction 1) and ferrocene (Reaction 4) in [Moepyrr][FAP] and [Emim][TCB] over the temperature range reported. The results in the peak potential differences are shown in Table 1, below, which shows that the peak potential difference for the structurally similar decamethylferrocene and ferrocene is essentially temperature independent.

Table 1: Peak potential differences of decamethylferrocene and ferrocene in [Moepyrr][FAP] and [Emim][TCB] at 298, 303 and 313 K. $\Delta E_{1/4}$ is defined as the difference between the redox potentials of decamethylferrocene and ferrocene, corresponding to Reactions 1 and 4.

Temperature / K	$\Delta E_{1/4}$ / V	
	(in [Moepyrr][FAP])	(in [Emim][TCB])
298	0.5737	0.5342
303	0.5737	0.5342
313	0.5736	0.5342

It is seen that $\Delta E_{1/3}$ and $\Delta E_{2/3}$ are both 'insensitive' to temperature change.

Example 3

To investigate these observations further similar experiments were performed with bisferrocene in a range of ionic liquids. Table 2, below, shows the peak potential differences for the first and second oxidation of bisferrocene in [Pmim][NTf₂], [Emim][TCB]

and [Moepyrr][FAP] over the temperature range of 298-313 K. It can be seen that all the peak differences increase with the temperature apart from in [Moepyrr][FAP].

Table 2: Peak potential differences of the first and second oxidation of bisferrocene in [Moepyrr][FAP] and [Emim][TCB] at 298, 303 and 313 K. $\Delta E_{2/3}$ is defined as the difference between the first and second oxidation potentials of bisferrocene (see Reactions 2 and 3).

Temperature / K	$\Delta E_{2/3}$ / V		
	(in [Moepyrr][FAP])	(in [Pmim][NTf ₂])	(in [Emim][TCB])
298	0.2202	0.2043	0.2077
303	0.2202	0.2052	0.2089
313	0.2202	0.2077	0.2110

Example 4

- Work by Barrosse-Antle et al. suggests that many dissolved gases, including N₂ the main component in air, may increase the diffusion coefficient of solutes in ionic liquids.³¹ This observation implies that decamethylferrocene and bisferrocene in [Moepyrr][FAP] in air may show different temperature dependence of peak potential difference as compared to the experiments under vacuum. Further investigation was therefore carried out in dried air. Before conducting experiments, the system was purged into air for more than 15 hours in order to equilibrate the humidity between the ionic liquid and air.

Figure 2a shows the square wave voltammetry for the oxidation of decamethylferrocene (peak 1) and bisferrocene (peaks 2 and 3) in [Moepyrr][FAP] under dried air (RH=1%).

- The corresponding plot of peak potential difference against temperature, between peaks 1 and 2, $\Delta E_{1/2}$, is displayed in Figure 2b. It is again observed that $\Delta E_{1/2}$ is insensitive to temperature change, where the equation for the line of best fit is given as below,

$$\Delta E_{1/2} = 0.5053 + 2 \times 10^{-7}T$$

Equation 2

where, T is the temperature in K.

Figure 2c depicts the peak potential difference $\Delta E_{1/3}$, measured between peak 1 and peak 3, as a function of temperature where a linear increase with temperature is seen. This temperature dependent peak potential difference can be described by the following equation,

$$\Delta E_{1/3} = 0.4327 + 0.9744 \times 10^{-3}T \quad \text{Equation 3}$$

5

A similar observation is made with the temperature relationship of peak potential difference between peak 2 and peak 3, of $\Delta E_{2/3}$, which is shown in Figure 2d. This linear relation is given below,

$$\Delta E_{2/3} = -0.0726 + 0.1121 \times 10^{-3}T \quad \text{Equation 4}$$

- 10 Comparing the gradients from Equations 3 and 4, it is observed that $\Delta E_{1/3}$ is more sensitive towards temperature change.

Example 5

(Temperature and humidity calibration using decamethylferrocene and bisferrocene)

15

Next the present inventors investigated the humidity effects as the temperature dependences of $\Delta E_{1/2}$ and $\Delta E_{1/3}$. The humidifier and its calibration were described in the experimental section. The humidity was controlled by carefully adjusting the wet and dry air flow rates. Before electrochemical analysis, humidified air was passed through the analytes for more than 15 hours to ensure that the humidity of the system has fully equilibrated. This was monitored by successive cyclic voltammetric scans for decamethylferrocene and bisferrocene in [Moepyrr][FAP] at a platinum micro electrode (a scan rate of 10 mV/s and an interval of 1 hour between scans) overnight. The variation in steady state current at different scans indicated whether the equilibrium has been reached. It was observed that the current in cyclic voltammetry reached a steady value after ca 15 hours. The oxidation of decamethylferrocene and bisferrocene at different humidities was characterised using square wave voltammetry.

Figure 3a depicts the plot of $\Delta E_{1/2}$ vs. temperature over the RH range of 1% to 50%, where $\Delta E_{1/2}$ is independent of temperature over the temperature and humidity range studied (i.e. $T = 298 - 318$ K and $RH = 1\% - 50\%$). It can be seen that $\Delta E_{1/2}$ changes with humidity but not with temperature at a fixed humidity.

30

Figure 3b shows $\Delta E_{1/3}$ as a function of temperature over the same humidity range. It can be seen that $\Delta E_{1/3}$ in the humidity range studied is linearly dependent on temperature. Table 3, below, shows the temperature dependence of $\Delta E_{1/3}$ for five representative values of relative humidity. It is observed that the temperature dependency varies only slightly for different humidities. These slight variations observed are predominately due to the influence of different levels of moisture on the formal potentials of the BisFc/ BisFc⁺ couples.

- 10 Table 3: Gradients and intercepts of plots of $\Delta E_{1/3}$ vs. temperature at different RH. $\Delta E_{1/3}$ is the peak potential difference of the oxidation of decamethylferrocene and second oxidation of bisferrocene in [Moepyr][FAP].

RH (%)	intercept (V)	gradient (mV)
1	0.6981	0.9744
12	0.7101	0.91313
25	0.70298	0.93313
35	0.7011	0.9090
50	0.7013	0.9196

Figure 4 shows the square wave voltammetry for DmFc and BisFc over a range of humidity at 298 K, where the potential axis has been shifted to show the potential relative to the DmFc/DmFc⁺ peak potential. The first oxidation and second oxidation of bisferrocene are enlarged and are shown in the inlays of Figure 4. A clear increase in the peak potential of BisFc/BisFc⁺ couple with humidity is observed whereas the potential change for BisFc⁺/BisFc²⁺ with humidity is less significant.

Figure 5 shows the plot of $\Delta E_{1/2}$ vs. RH where the former is the average at a fixed temperature and error bars are assigned using standard deviation methods for each set of data. It shows that $\Delta E_{1/2}$ increases with RH (over a temperature range of 298K to 318 K) in a 2nd order polynomial manner and the relation is described below,

$$\Delta E_{1/2} = 0.505 + 8.181 \times 10^{-5} RH + 5.997 \times 10^{-7} RH^2 \quad \text{Equation 5}$$

Figure 6 depicts the plots of $\Delta E_{1/3}$ versus RH at 298, 303, 308, 313 and 318 K. From this figure, it is seen that $\Delta E_{1/3}$ slightly increases with RH at 298 K and the difference between the maximum and minimum values is approximately 1.5 mV while at 303 K, this difference reduces to 0.9 mV. For temperature at and above 308 K, $\Delta E_{1/3}$ is almost independent of temperature.

The average value of $\Delta E_{1/3}$ is plotted against temperature in Figure 7. The bars in the figure represent the uncertainty at each temperature.

$$\Delta E_{1/3} = 0.31844 + 0.9181 \times 10^{-3} T \quad \text{Equation 6}$$

Example 6

(Simultaneous determination of temperature and humidity)

Figure 10 illustrates the proposed method for determining precise values of humidity and temperature simultaneously. First, $\Delta E_{1/3}$ can be read from square wave voltammetry and the temperature value can be roughly estimated by substituting the $\Delta E_{1/3}$ into Equation 6. For example, an uncertainty of 3 K is expected for temperature around 298 K. Then the relative humidity can be estimated using $\Delta E_{1/2}$, the peak potential difference of peaks 1 and 2, and Equation 5 and an approximation of $\pm 2\%$ RH at each humidity value should be taken into account. Next, it is known that at a fixed humidity, the relationship of $\Delta E_{1/3}$ and temperature is one-to-one; hence a more precise value of temperature can be evaluated. Given a more accurate temperature value is known, a better estimate of the humidity can be made. Finally, the quality of the estimate is tested via the comparison of the new estimates of temperature and humidity with the old ones. If these two values are very close, it can be concluded that the estimates are representative of the actual temperature and humidity values; if not, the estimates can be further improved by repeating the same process iteratively until the estimates do not change by an appreciable amount.

Conclusions

Through square wave voltammetric analysis of bisferrocene and decamethylferrocene system, the present inventors measured the temperature dependences of two

independent peak potential differences, $\Delta E_{1/2}$ (i.e. the potential difference for oxidation of decamethylferrocene and first oxidation of bisferrocene) and $\Delta E_{1/3}$ (i.e. the potential difference for oxidation of decamethylferrocene and second oxidation of bisferrocene). The former is temperature insensitive and the other has a temperature coefficient of 0.92 mV/K. The humidity effects of these two independent pairs over the temperature range of 298K to 318K have been investigated. It has observed that the peak potential difference between $\text{DmFc}/\text{DmFc}^+$ and $\text{BisFc}/\text{BisFc}^+$ is humidity dependent and the peak potential differences of other pairs is less influenced by humidity change. A method for finding accurate values of humidity and temperature has been proposed.

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5

The above references are incorporated herein by reference in their entirety.

CLAIMS

1. An electrochemical method for measuring humidity, the method comprising:
determining, at a humidity of interest, a first potential at which a first electrochemical reaction occurs;
determining, at the humidity of interest, a second potential at which a second electrochemical reaction occurs;
determining the difference between the first and second potentials;
converting the difference between the first and second potentials to a value of humidity.
2. An electrochemical method for measuring temperature and humidity, the method comprising the electrochemical method for measuring humidity according to claim 1,
and further comprising an electrochemical method for measuring temperature comprising:
determining, at a temperature of interest, a third potential at which a third electrochemical reaction occurs;
determining, at the temperature of interest, a fourth potential at which a fourth electrochemical reaction occurs;
determining the difference between the third and fourth potentials;
converting the difference between the third and fourth potentials to a value of temperature.
3. The electrochemical method according to claim 2, wherein the first electrochemical reaction and third electrochemical reaction are the same as one another.
4. The electrochemical method according to claim 3, wherein the second electrochemical reaction and fourth electrochemical reactions are different to one another.
5. The electrochemical method according to any one of claims 2 to 4, wherein the first, second, third and fourth potentials are measured at the same working electrode.
6. The electrochemical method according to any one of claims 2 to 5, wherein the difference between third and fourth potentials is dependent on humidity and/or the difference between first and second potentials is dependent on temperature, and
(i) the value of temperature initially obtained in accordance with claim 2 is used to recalculate the value of humidity and/or

(ii) the value humidity initially obtained in accordance with claim 1 is used to recalculate the value of temperature.

7. The electrochemical method according to any one of claims 2 to 5, wherein the difference between third and fourth potentials is dependent on humidity, and the electrochemical method for measuring temperature is carried out a first time in which the converting of the difference between the third and fourth potentials to a value of temperature uses a relationship between known temperatures and the difference between third and fourth potentials at an predetermined humidity to obtain a first value in temperature,

and the measured value of humidity obtained in the electrochemical method in accordance with claim 1 is then used to recalculate the value of temperature, using a relationship between known temperatures and the difference between third and fourth potentials at the measured value of humidity,

and the first value in temperature and recalculated value of temperature are compared with one another.

8. The electrochemical method according to claim 6 or claim 7, wherein the recalculation is repeated until the difference between recalculated values of temperature and/or recalculated values of humidity is/are below a predetermined threshold.

9. The electrochemical method according to any one of the preceding claims, wherein the first electrochemical reaction involves a change in oxidation state of an atom in a first species, and the second electrochemical reaction involves a change in oxidation state of an atom in a second species, with the first and second species being different to one another, and the atoms being oxidised or reduced in first and second species being the same as one another and in the same coordination environment.

10. The electrochemical method according claim 9, wherein the change of oxidation state of the atom in the first and second electrochemical reactions is from a first oxidation state to a second oxidation state, the first oxidation state is the same in the first and second electrochemical reactions, and the second oxidation state is the same in the first and second electrochemical reactions.

11. The electrochemical method according to claim 10, wherein the electrochemical method further comprises the electrochemical method for measuring temperature according to claim 2, wherein the first and third electrochemical reactions are the same as one another,

and the fourth electrochemical reaction involves further oxidation or reduction of the species produced by the oxidation or reduction of the second species in the second electrochemical reaction.

12. The electrochemical method according to any one of claims 9 to 11, wherein the first species comprises a ferrocene containing a single iron atom, and the second species comprises a multiferrocene compound.

13. The electrochemical method according to any one of the preceding claims, wherein the converting the difference between the first and second potentials is carried out by using the Formula (b)

$$E_{2/1} = C + nRH + o(RH)^2 \quad \text{Formula (b)}$$

wherein $E_{2/1}$ is the difference between the first and second potentials, and C is a constant, n is a coefficient and o is a coefficient, with C, n and o having been determined in a calibration step, and RH is the value of humidity.

14. The electrochemical method according to any one of the preceding claims, wherein the first and second potentials are formal potentials determined by a pulse voltammetry method.

15. The electrochemical method according to any one of the preceding claims, wherein the first and second potentials are determined by a square wave voltammetry method in which peaks in current are seen at each of the first potential and second potentials.

16. The electrochemical method according to any one of the preceding claims, wherein the first and second electrochemical reactions are carried out in an ionic liquid.

17. The electrochemical method according to claim 16, wherein the viscosity of the ionic liquid varies with a change in atmospheric humidity.

18. The electrochemical method according to claim 16 or claim 17, wherein the ionic liquid has a dynamic viscosity, as measured at 20 °C, of at least 50 cP.

19. The electrochemical method according to claim 16 or claim 17, wherein the ionic liquid has a dynamic viscosity, as measured at 20 °C, of at least 100 cP.
20. The electrochemical method according to claim 16 or claim 17, wherein the ionic liquid has a dynamic viscosity, as measured at 20 °C, of at least 150 cP.
21. The electrochemical method according to any one of claims 16 to 20, wherein the ionic liquid comprises a perfluorinated alkyl fluorophosphate anion.
22. The electrochemical method according to any one of claims 16 to 21, wherein the ionic liquid comprises a tris(pentafluoroethyl)trifluorophosphate anion.
23. The electrochemical method according to any one of claims 16 to 22, wherein the method also involves measuring temperature in accordance with claim 2, and the third and fourth reactions are carried out in the same ionic liquid as the first and second reactions.
24. The electrochemical method according to any one of the preceding claims, wherein the method is carried out in an electrochemical sensor.
25. The electrochemical method according to claim 24, wherein the method further comprises using the electrochemical sensor to sense and/or obtain information on the concentration of a species within the electrochemical sensor other than a species involved in the first and/or second (and, if carried out, the third and/or fourth) electrochemical reactions.
26. The electrochemical method according to claim 24 or claim 25, wherein the electrochemical sensor is a gas sensor.
27. A humidity sensor, wherein the sensor is adapted to:
 - determine, at a humidity of interest, a first potential at which a first electrochemical reaction occurs;
 - determine, at the humidity of interest, a second potential at which a second electrochemical reaction occurs;
 - determine the difference between the first and second potentials;
 - convert the difference between the first and second potentials to a value of humidity.

28. A humidity sensor according to claim 27 that is also a temperature sensor, wherein the sensor is further adapted to:

determine, at a temperature of interest, a third potential at which a third electrochemical reaction occurs;

determine, at the temperature of interest, a fourth potential at which a fourth electrochemical reaction occurs;

determine the difference between the third and fourth potentials;

convert the difference between the third and fourth potentials to a value of temperature.

29. A humidity sensor according to claim 27 or claim 28 that is further adapted to carrying out the method according to any one of claims 3 to 26.

30. An electrochemical sensor for sensing a species, the sensor comprising:

a working electrode, a counter electrode and a carrier medium in contact with the working electrode and the counter electrode, wherein the carrier medium contains, and/or the working electrode has immobilised on a surface thereof, a ferrocene compound containing a single iron atom and a multiferrocene compound, and the carrier medium is an ionic liquid having a dynamic viscosity, as measured at 20 °C, of at least 50 cP.

31. An electrochemical sensor for sensing a species according to claim 30, wherein the ionic liquid has a dynamic viscosity, as measured at 20 °C, of at least 100 cP.

32. The electrochemical method according to claim 30 or 31, wherein the ionic liquid comprises a perfluorinated alkyl fluorophosphate anion.

33. The electrochemical method according to any one of claims 30 to 32, wherein the ionic liquid comprises a tris(pentafluoroethyl)trifluorophosphate anion.

FIG. 1

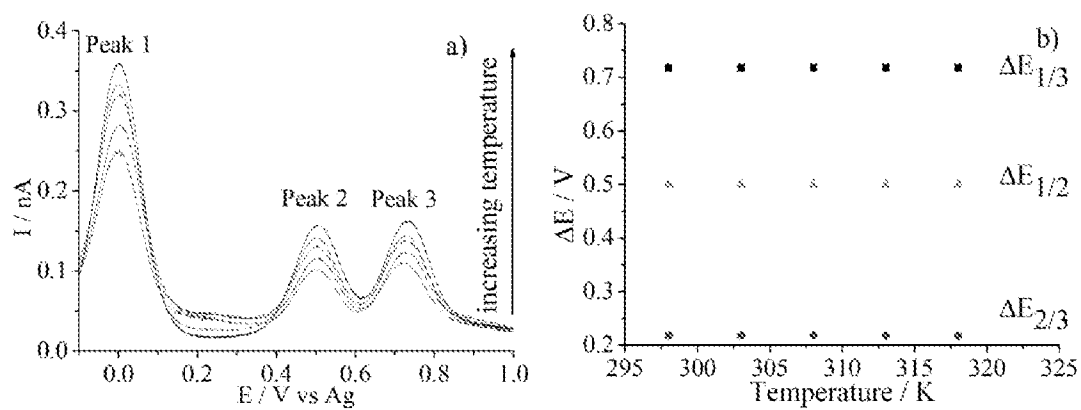


FIG. 2

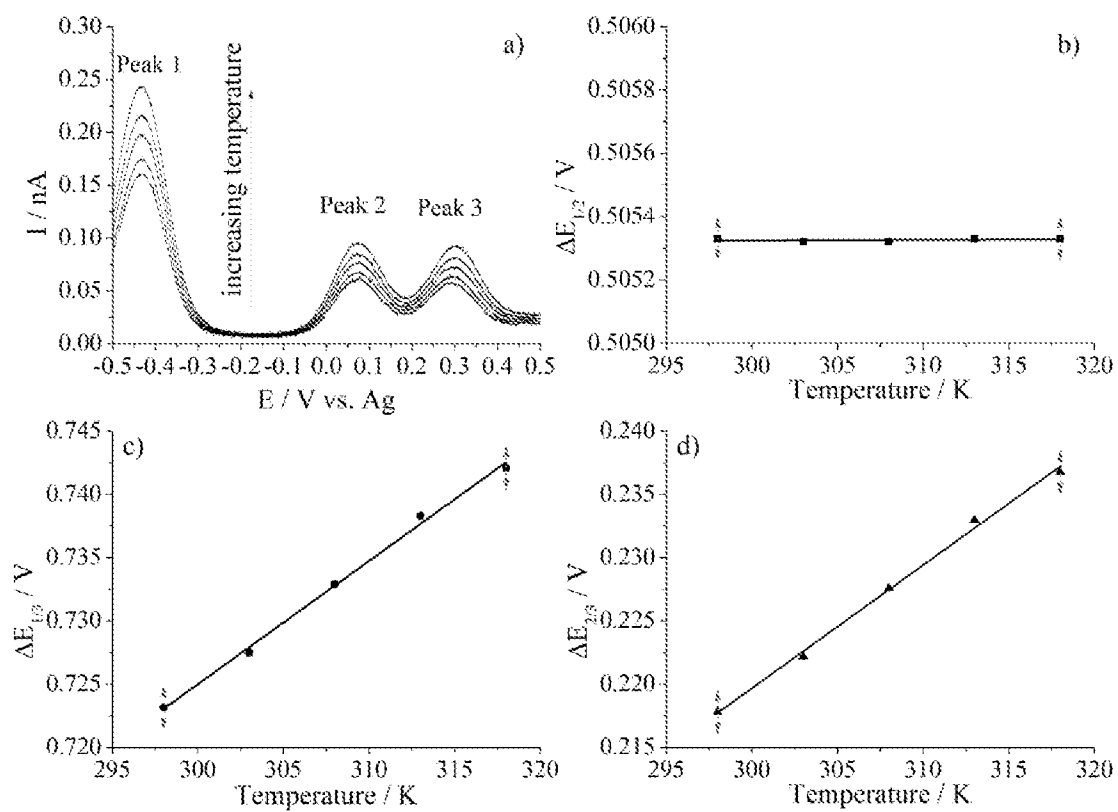


FIG. 3

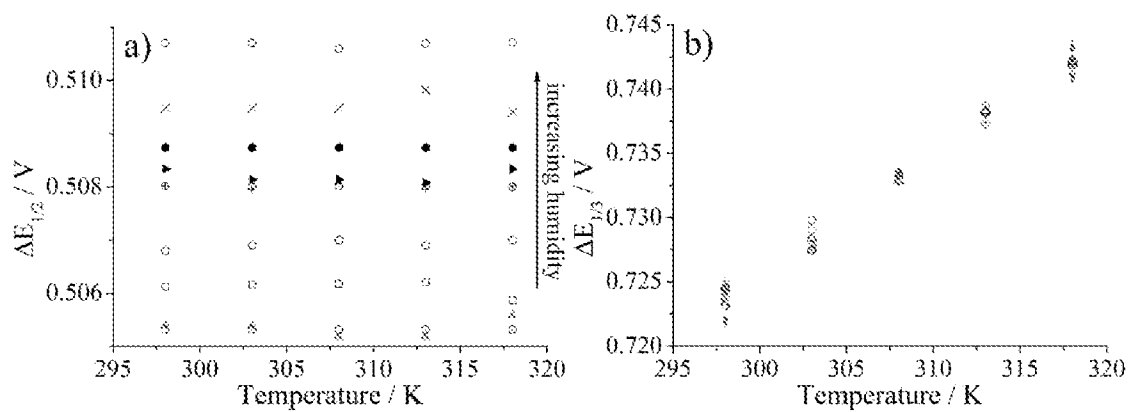


FIG. 4

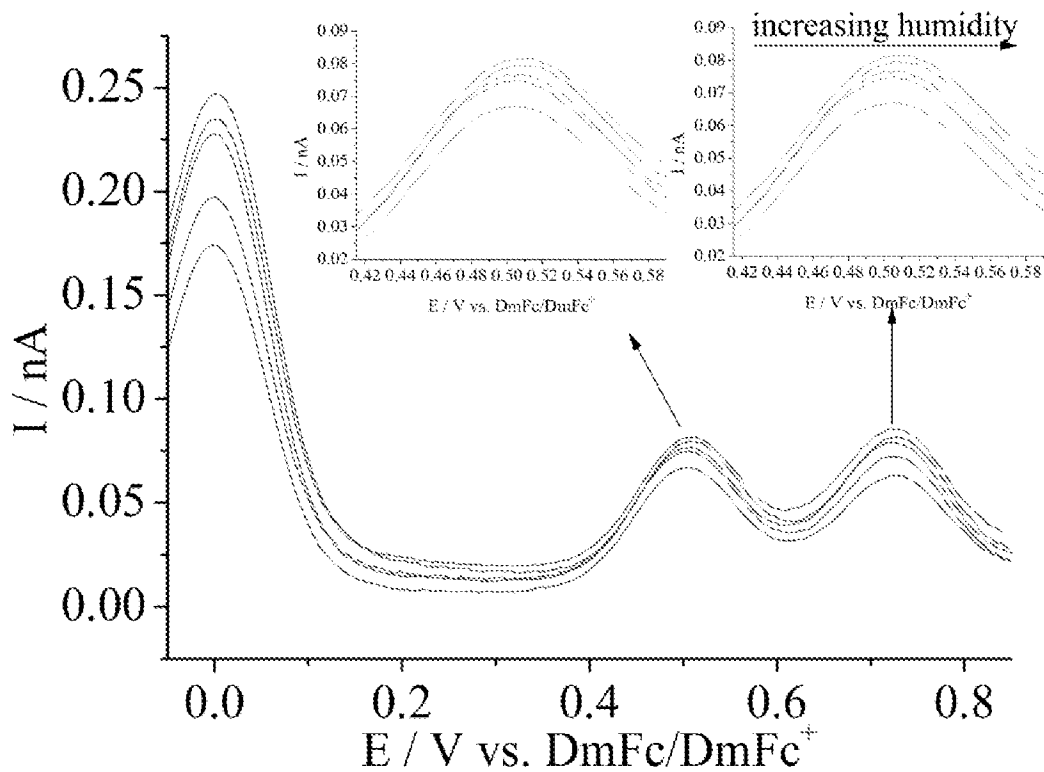


FIG. 5

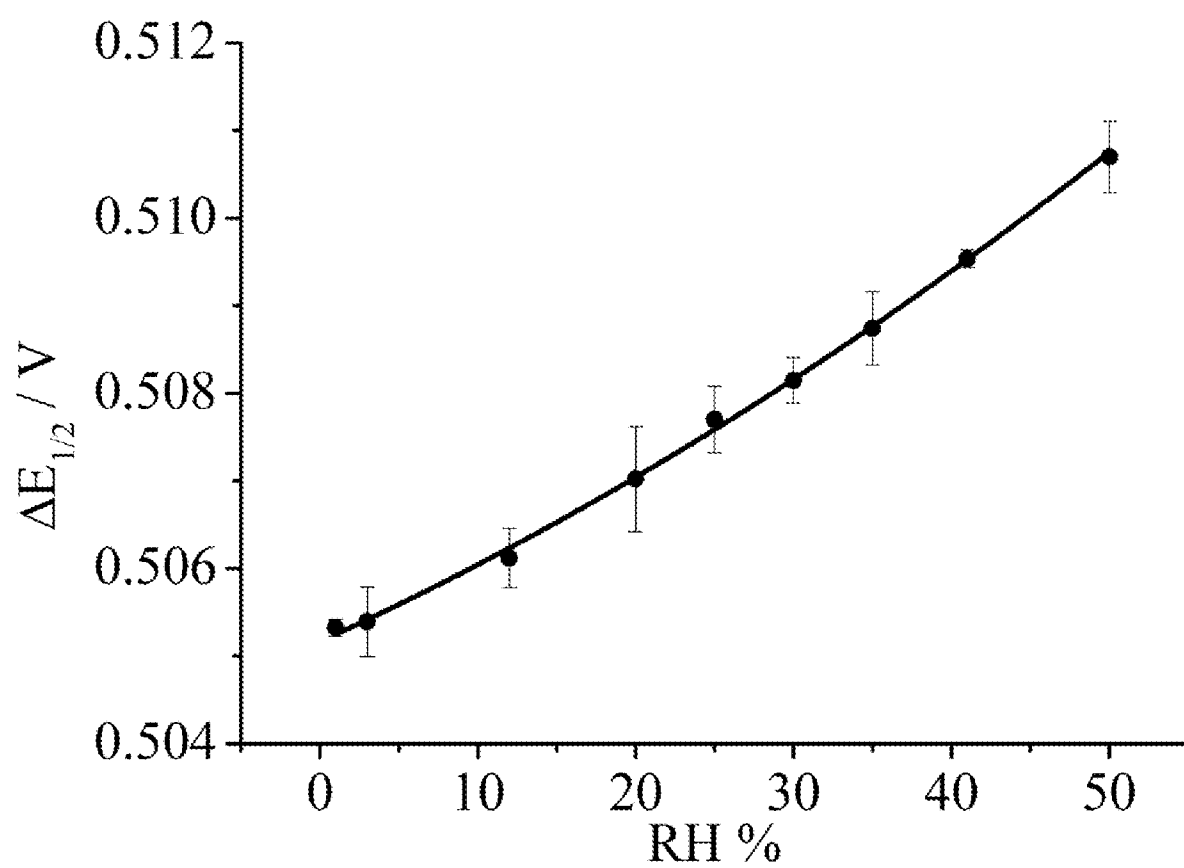


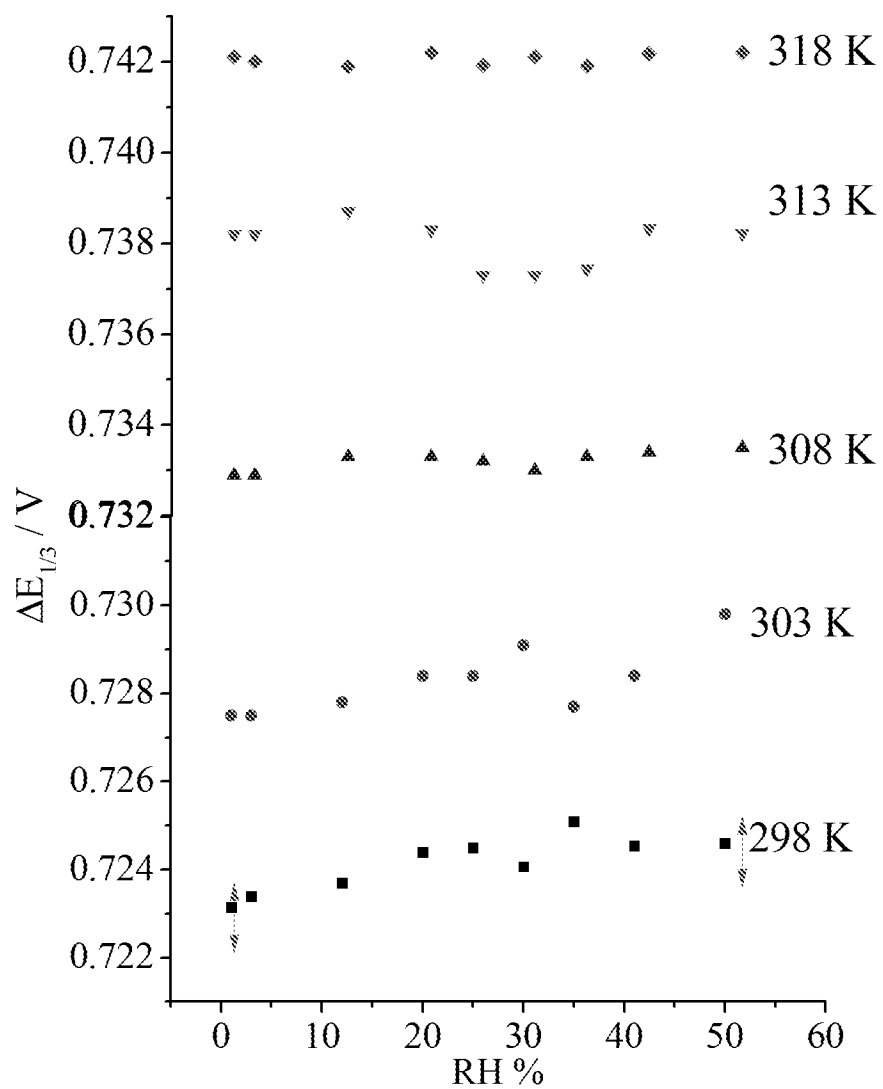
FIG. 6

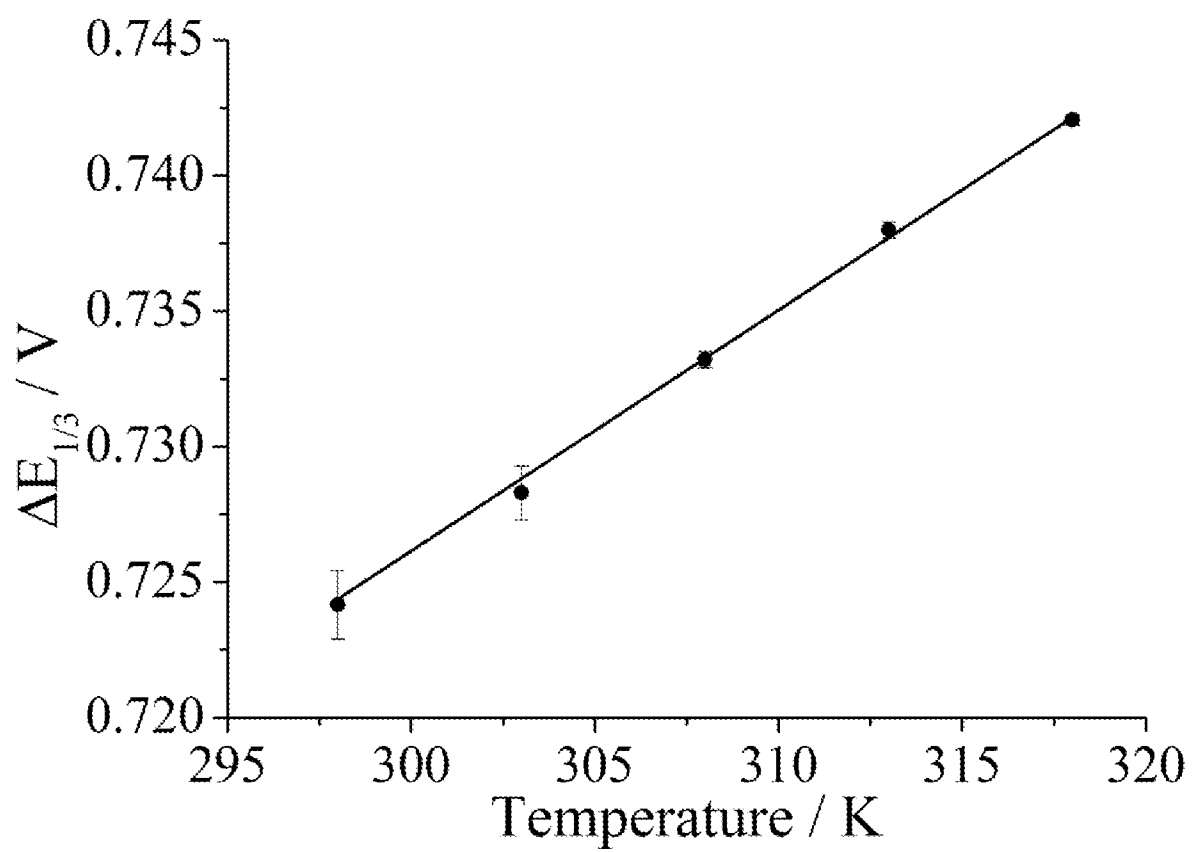
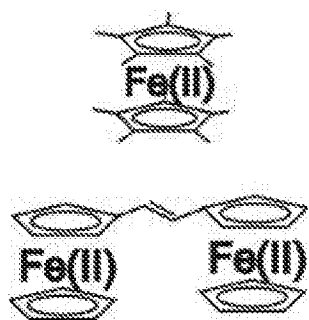
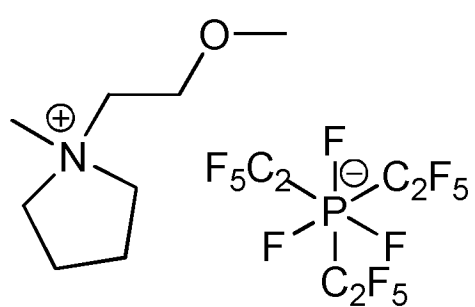
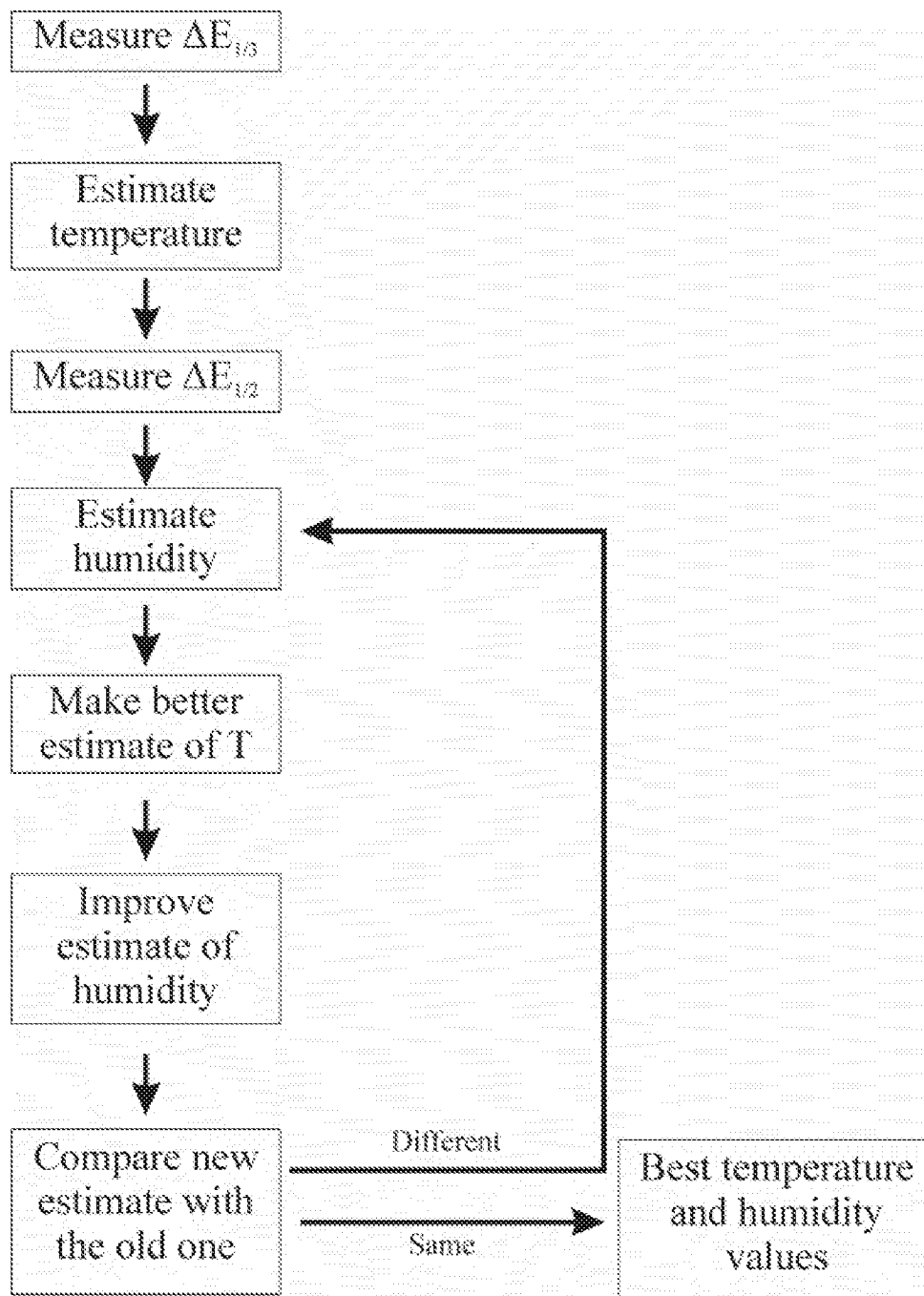
FIG. 7**FIG. 8****FIG. 9**

FIG. 10



INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2013/052060

A. CLASSIFICATION OF SUBJECT MATTER

INV. G01N27/48
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G01N

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	LINHONGJIA XIONG ET AL: "Tuning solute redox potentials by varying the anion component of room temperature ionic liquids", CHEMICAL COMMUNICATIONS, vol. 48, no. 46, 20 April 2012 (2012-04-20), pages 5784-5786, XP055085959, ISSN: 1359-7345, DOI: 10.1039/c2cc32308g	30-33
A	the whole document ----- -/--	1-29

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents :

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"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

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Date of the actual completion of the international search

31 October 2013

Date of mailing of the international search report

07/11/2013

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Authorized officer

Klein, Marc-Oliver

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2013/052060

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	ANGEL A.J. TORRIERO ET AL: "Ionic liquid effects on the redox potential of ferrocene", ELECTROCHEMISTRY COMMUNICATIONS, vol. 16, no. 1, 15 December 2011 (2011-12-15), pages 84-87, XP055086000, ISSN: 1388-2481, DOI: 10.1016/j.elecom.2011.12.006 the whole document -----	1-33
A	LINHONGJIA XIONG ET AL: "An electrochemical thermometer: voltammetric measurement of temperature and its application to amperometric gas sensing", THE ANALYST, vol. 137, no. 11, 10 April 2012 (2012-04-10), pages 2567-2573, XP055085577, ISSN: 0003-2654, DOI: 10.1039/c2an35336a the whole document -----	1-33
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T	MENGDI ZHANG ET AL: "A hydrogel modified electrode for application as a voltammetric temperature sensor and its use in oxygen detection", ANALYTICAL METHODS, vol. 5, no. 14, 3 June 2013 (2013-06-03), page 3473, XP055085581, ISSN: 1759-9660, DOI: 10.1039/c3ay40741a the whole document -----	