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- (71) **Applicant:** CORNELL UNIVERSITY [US/US]; Cornell Center For Technology Licensing ("CTL"), At Cornell University, 395 Pine Tree Road, Suite 310, Ithaca, NY 14850 (US).
- (72) **Inventors:** ABRUNA, Hector D.; 101 Thurton Ave., Ithaca, NY 14850 (US). VAN DOVER, Robert, Bruce; 1 Strawberry Lane, Ithaca, NY 14850 (US). VAN WASSEN, Abigail R.; 1132 E. Witt Street, Philadelphia, PA 19125 (US).
- (74) **Agents:** WATT, Rachel S. et al.; Hodgson Russ LLP, The Guaranty Building, 140 Pearl Street, Suite 100, Buffalo, NY 14202-4040 (US).

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(54) **Title:** COPPER PALLADIUM COMPOSITIONS AS OXIDATION AND REDUCTION CATALYSTS

(57) **Abstract:** The copper-palladium compositions can be used as reduction or oxidation catalysts. The copper-palladium compositions can be in the form of, for example, nanoparticles or thin films. The copper-palladium compositions can be used in reduction and/or oxidation methods. The copper-palladium compositions can be used in devices such as, for example, catalytic converters, industrial scrubbers, electrolyzers and fuel cells.



COPPER-PALLADIUM COMPOSITIONS AS OXIDATION AND REDUCTION CATALYSTS

CROSS-REFERENCE TO RELATED APPLICATIONS

- 5 **[0001]** This application claims priority to U.S. Provisional Application No. 62/194,001, filed on July 17, 2015, the disclosure of which is hereby incorporated by reference.

FIELD OF THE DISCLOSURE

- 10 **[0002]** The disclosure generally relates to copper-palladium compositions. More particularly the disclosure generally relates to copper-palladium compositions that can be used as oxidation or reduction catalysts.

BACKGROUND OF THE DISCLOSURE

- 15 **[0003]** As a 4-e- reaction, there is a significant kinetic barrier (“overpotential”) to catalyzing the oxygen-reduction reaction (ORR). This leads to a decrease in fuel cell voltage and overall efficiency. Oxygen reduction has two possible reaction pathways leading to water (4-electron reduction) and hydrogen peroxide (2-electron reduction), further complicating the reaction. HO₂⁻ (generated from hydrogen peroxide) can oxidize a membrane, degrading it. Traditionally, oxygen-reduction catalysts have been Pt-based. However, Pt is expensive and alkaline conditions may allow other metals to act as a catalyst.

- 20 **[0004]** While some Pd alloy catalysts have been tested under acidic conditions, the differences in surface state/stability as well as the different ions in solution that would be present at different pH's can have an impact on catalysis and even lead to different reaction mechanisms.

- 25 **[0005]** Pd has been used as an alkaline oxygen-reduction catalyst. However, Pd is still relatively expensive. A way to lower the cost of a catalyst using Pd, such as by reducing the amount/fraction of Pd, would be desirable.

- 30 **[0006]** Previous work on the CuPd system has been limited to acidic media or to catalytic applications that do not involve oxygen reduction. Also, previous work on CuPd (and PtCu) in acid (including Nafion-based PEM fuel cells and systems) has involved the deliberate “dealloying” or dissolution of the Cu to create a Pt- or Pd-rich shell.

- [0007]** Based on the foregoing, there is a need for improved oxidation or reduction catalysts.

SUMMARY OF THE DISCLOSURE

[0008] The present disclosure provides copper-palladium compositions and uses thereof. The compositions can be used, for example, in methods of reducing or oxidizing various chemical entities.

5 [0009] In an aspect, the present disclosure provides an oxidation and/or reduction catalyst. The catalyst is a CuPd composition. This catalyst can be in the form of a thin film or a nanoparticle. The catalysts reduce, for example, oxygen, or carbon dioxide ions and/or oxidize, for example, methanol, ethanol, or hydrogen ions. These reductions and/or oxidations can be carried out in an alkaline medium. In various examples, the percentage of
10 Pd is from 5 to 65 atom% or 10 to 65 atom%, including all integer atom% values and ranges therebetween. The CuPd compositions may have additional metal components. For example, the composition can be a ternary composition.

[0010] The CuPd composition can be a nanoparticle, a thin film, or in some other form. The nanoparticles are, for example, 1 to 50 nm in diameter, including all integer nm
15 values and ranges therebetween. The thin films are, for example, 5 to 100 nm in thickness, including all integer nm values and ranges therebetween. Thin films with the CuPd catalyst can be disposed on various substrates.

[0011] In various aspects, the present disclosure provides CuPd compositions used in reduction methods and/or oxidation methods. In the methods, one or more CuPd composition
20 is a reduction catalyst and/or an oxidation catalyst. CuPd compositions (e.g., a thin films or nanoparticles) can be used, for example, for the reduction of oxygen or carbon dioxide or for the oxidation of methanol, ethanol, or hydrogen. The CuPd compositions can also be used for formic acid oxidation or other organic oxidation processes. Such reactions can be performed in, for example, a catalytic converter, industrial scrubber, electrolyzer or fuel cell.

25 [0012] In an aspect, the present disclosure provides devices comprising CuPd compositions. For example, a device is a catalytic converter, industrial scrubber, electrolyzer or fuel cell, where one or more electrode (cathode and/or anode) of the device comprises a one or more CuPd composition.

BRIEF DESCRIPTION OF THE FIGURES

30 [0013] For a fuller understanding of the nature and objects of the disclosure, reference should be made to the following detailed description taken in conjunction with the accompanying drawings, in which:

FIG. 1 is a cross-sectional diagram of an example of a CuPd alkaline oxygen-reduction

catalyst formed in accordance with an example of this disclosure;

FIG. 2 is a graph showing Eonset versus atom% Pd including current cost values of Pd;

FIG. 3 is a graph showing Eonset versus atom% Pd including current cost values of Pd;

FIG. 4 is a graph comparing j (current density) versus E for Pt, Pd, Cu, and CuPd;

5 FIG. 5 is a graph comparing j (current density) versus E for various Pd compositions;

FIG. 6 is a diagram of an exemplary fuel cell including a catalyst; and

FIG. 7 is a graphical representation of X-ray diffraction (XRD) data showing that examples of the copper-palladium compositions are alloyed phases with the same crystal structure as both Pd and Cu as demonstrated by the peak shifting continuously from the Pd-rich value to
10 the Cu-rich value.

DETAILED DESCRIPTION OF THE DISCLOSURE

[0014] Although claimed subject matter will be described in terms of certain embodiments and examples, other embodiments and examples, including embodiments and examples that do not provide all of the benefits and features set forth herein, are also within
15 the scope of this disclosure. Various structural, logical, and process step changes may be made without departing from the scope of the disclosure.

[0015] Ranges of values are disclosed herein. The ranges set out a lower limit value and an upper limit value. Unless otherwise stated, the ranges include all values to the magnitude of the smallest value (either lower limit value or upper limit value) and ranges
20 between the values of the stated range. In various examples, all ranges provided herein include all values that fall within the ranges to the tenth decimal place, unless indicated otherwise.

[0016] The present disclosure provides copper-palladium compositions and uses thereof. The copper-palladium compositions can also be referred to as palladium-copper
25 (PdCu) compositions. The compositions can be used, for example, in methods of reducing or oxidizing various chemical entities.

[0017] Copper-Palladium compositions of the present disclosure, which can be used as catalysts, are unusual because of the approach. Typically, metal catalysts with a noble, expensive (and very catalytically-active) metal such as Pd are considered to be the catalytic
30 metal in a binary (or ternary, quaternary, etc.) catalyst. Because metal at the surface of the catalyst particle or film is accessible and able to act as a catalyst, the approach is most commonly to “dealloy”, or dissolve, the less noble, more inexpensive metal (in this case the Cu) to leave behind a spongy or porous outer shell that is enriched in the more noble metal

(such as Pd or Pt). This shell can have a higher surface area to volume ratio because it's porous, but it also segregates the more noble metal to the surface. With this approach, you might expect that as you add the more noble metal (e.g., Pd or Pt) to the less noble metal, you'd get a linear increase in the activity until you reached the maximum, probably at very high percentages of the noble metal, if not entirely that metal.

[0018] However, with respect to the CuPd compositions of the present disclosure, that is not what was observed. It was surprisingly and unexpectedly found that addition of 10% Pd increases the onset potential by almost 200 mV, a value that is just 20 mV worse than that of pure Pd and 30 mV worse than pure Pt under these same conditions, or a difference of 2 to 3%. In the CuPu system, the Cu is not observed to dissolve by XPS and leave behind a Pd-rich shell. Instead, the surface actually enriches in Cu, and the Cu metal (as opposed to the Cu oxide) appears to be stabilized by the addition of the Pd, which can account for the beneficial effect on the catalysis seen even at 10 atom% Pd. (The oxide can inhibit the reduction of oxygen.) Furthermore, at increasingly high percentages of Pd, the activity of the CuPd composition starts to decline.

[0019] In an aspect, the present disclosure provides an oxidation and/or reduction catalyst. The catalyst is a CuPd composition. This catalyst can be in the form of a thin film or a nanoparticle.

[0020] The catalysts reduce, for example, oxygen, or carbon dioxide ions and/or oxidize, for example, methanol, ethanol, or hydrogen ions. In various examples, a CuPd composition is an oxygen-reduction catalyst, methanol-oxidation catalyst, ethanol-oxidation catalyst, carbon dioxide-reduction catalyst, or hydrogen-oxidation catalyst.

[0021] CuPd is, for example, an active oxygen-reduction catalyst in alkaline medium. With respect to its "onset potential" (voltage) for the ORR, CuPd is better (i.e., more positive onset) than the "standard" catalyst, Pt (see FIGs. 2-3). Additionally, by examining the catalytic activity (given by the onset potential, which relates to the maximum voltage of a fuel cell, or the open circuit voltage of such a cell, that could be made with the catalyst) as a function of the percentage of Pd in the catalyst, there is a point where a desirable level of activity is achieved. For example, desirable activity may be observed at 50-60 Pd atom %, though other ranges or integer % values are possible.

[0022] As seen in FIGs. 4-5, the CuPd composition outperforms other Pd compositions. CuPd had an E_{onset} of 0.92, versus 0.89 for Pt, 0.88 for Pd, 0.9 for PdAu, 0.84 for PdAg, and 0.86 for PdRh. Furthermore, CuPd has the lowest cost for a film of similar size

of any of those Pd compositions. The cost of a CuPd film is 50% the cost of a similar Pd catalyst and 30% the cost of a similar Pt catalyst.

[0023] CuPd compositions include $\text{Pd}_x\text{Cu}_{1-x}$, where $0 < x < 1$ (referring to overall composition ratios, in atomic fraction). In various examples, the percentage of Pd is from 5 to 65 atom% or 10 to 65 atom%, including all integer atom% values and ranges therebetween. In various other examples, the percentage of Pd is from 15 to 65 atom%, including all integer atom% values and ranges therebetween. In still various other examples, the percentage Pd is from 50 to 60 atom%. Without intending to be bound by any particular theory, it is considered that a Pd percentage in the composition from 50 to 60 atom% provides the most catalytic activity as an alkaline-oxygen reduction catalyst. Furthermore, Pd is more durable than Cu and increased Pd may result in better durability for the nanoparticles or thin film.

[0024] Usually the catalytic activity of an alloy or composition is approximately the average of the activities of the two parent metals. The activity of CuPd is surprisingly and unexpectedly better than either Cu or Pd, as shown in FIG. 4.

[0025] In yet another example, the percentage Pd is from 20 to 30 atom%. Pd from 20 to 30 atom% has comparable activity to Pt or Pd catalysts under similar conditions, but is cheaper to manufacture due to lower Pd content (e.g., atom percent composition). In another example, Pd_3Cu_2 (i.e., Pd 60 atom% and Cu 40 atom%) is formed.

[0026] The CuPd compositions are solid solutions although “ordered phases” are also possible. The compositions are homogeneous. For example, the compositions do not have Pd and/or Cu domains that are observable with methods known in the art. In various examples, the compositions are alloyed. They are not an ordered intermetallic phase. The CuPd film may be polycrystalline as determined by x-ray diffraction. The compositions can exhibit a crystal structure consistent with the body-centered cubic structure characteristic of both endmember elements, though superlattice ordering is not excluded.

[0027] CuPd compositions may have additional metal components. For example, a CuPd composition is a ternary composition. Ternary compositions including, but not limited to, CuPdAg, CuPdAu, CuPdCo, CuPdFe, and CuPdNi are within the scope of the disclosure because the catalytic activity of Ag, Au, Co, Fe and Ni, among other elements, is expected to further enhance the activity of the resulting ternary composition. Other metals or precious metals besides Ag, Au, Co, Fe or Ni can be used in a ternary composition with Pd and Cu. The ternary component (e.g., Ag, Au, Co, Fe, Ni, etc.) may be from 1 to 15 atom% of the ternary composition, including all integer atom% ranges and values therebetween.

[0028] A CuPd composition can be a nanoparticle, a thin film, or in some other form. The nanoparticles are, in various examples, 1 to 50 nm in diameter, including all integer nm values and ranges therebetween. For example, the nanoparticle is 1 to 15 nm in diameter. The nanoparticles can be made by methods known in the art.

5 **[0029]** Thin films are, in various examples, 5 to 100 nm in thickness, including all integer nm values and ranges therebetween. In several examples, the thin film is 10 to 50 nm in thickness or 50 nm in thickness.

[0030] Thin films can be formed by sputtering. The CuPd compositions also can be made using other deposition methods, including, but not limited to, physical vapor deposition techniques, such as pulsed laser deposition (PLD), or evaporation. The CuPd compositions can also be formed using chemical vapor deposition (CVD) techniques. The CuPd compositions can also be made as nanoparticles using co-precipitation methods, involving dissolving Pd and Cu salts, and then co-reducing them. These may be synthesized in the presence of carbon black, a catalyst support. They could also be made as bulk materials
10 (sheets, slugs, powders, etc.) from the metals themselves using high temperature, solid-state chemical or metallurgical methods. CuPd also can be made using other methods known to those skilled in the art.

[0031] Thin films with the CuPd catalyst can be disposed on various substrates. Thin films with the CuPd catalyst can be formed on, for example, a carbon black or glassy carbon
20 substrate with an optional adhesive (or “sticking”) layer, which provides adhesion between and the CuPd thin film and the substrate. Examples of suitable substrates include, but are not limited to, carbon supports (e.g., carbon black, glassy carbon), carbides, silicon, nitrides, and oxides). The substrate can be planar or non-planar. Examples of suitable adhesive layers include, but are not limited to, titanium, tantalum, and chromium.

25 **[0032]** In an aspect, the present disclosure provides CuPd compositions used in reduction methods. In the methods, one or more CuPd composition is a reduction catalyst. In another aspect, the present disclosure provides CuPd compositions used in oxidation methods. In the methods, one or more CuPd composition is an oxidation catalyst.

[0033] A CuPd composition (e.g., a thin film or nanoparticle) in accordance with the
30 present disclosure can be used for an oxidation reaction or a reduction reaction. The CuPd composition (e.g., a thin film or nanoparticle) in accordance with the present disclosure can be used for the reduction of oxygen or carbon dioxide or for the oxidation of methanol, ethanol, or hydrogen. A CuPd composition (e.g., a thin film or nanoparticle) in accordance with the present disclosure can be used for formic acid oxidation or other organic oxidation

processes. Other reduction and oxidation reactions can be performed and these are listed as examples. Such reactions can be performed in, for example, a catalytic converter, industrial scrubber, electrolyzer or fuel cell.

[0034] In an example, a method of oxidizing or reducing oxygen, carbon dioxide, or hydrogen ions comprises contacting a CuPd composition (e.g., a thin film or nanoparticle) with oxygen, carbon dioxide, or hydrogen ions (e.g., in gas form, liquid form, or in either form with an inert gas carrier or liquid carrier) under conditions such that at least part or all of the oxygen, carbon dioxide, or hydrogen ions are reduced or oxidized. The method may be carried out under alkaline conditions. The identification of suitable conditions for the reduction is within the purview of one having skill in the art.

[0035] Without intending to be bound by any particular theory, with respect to oxygen reduction it is considered that two reaction products and pathways are possible. Under alkaline condition, the incomplete reduction consumes 2 electrons and generates hydroxide (OH^-) and hydro-peroxide (HO_2^-). The complete reduction consumes 4 electrons and generates four equivalents of hydroxide. The hydro-peroxide generated by the 2 electron reaction can oxidize and degrade the membrane in a fuel cell and lead to a decline in fuel cell performance over time. Under alkaline conditions, Pt—the most common oxygen reduction catalyst—produces significant amounts of hydro-peroxide.

[0036] In examples, the CuPd compositions act as 4-electron catalysts or about 4-electron catalysts. By “about” 4-electron catalysts it is meant that the CuPd compositions act as 3.5 or greater electron catalysts. In various examples, a CuPd composition acts as at least a 3.5 electron or greater, 3.6 electron or greater, 3.7 electron or greater, 3.8 electron or greater, or 3.9 electron or greater catalyst. In these examples, the CuPd compositions can be oxygen reduction catalysts.

In catalytic reactions (e.g., catalytic reduction of oxygen), a CuPd composition can generate less hydro-peroxide than a Pt catalyst under the same conditions. It is expected that reduced amounts of hydro-peroxide can lead to improved long-term performance of a device (e.g., a fuel cell) which incorporates a CuPd composition as a catalyst. In various examples, in a catalytic reaction (e.g., catalytic reduction of oxygen) the CuPd compositions produce 10% or less hydro-peroxide, 5% or less hydro-peroxide, or 1% or less hydro-peroxide. In another example, in a catalytic reaction the CuPd compositions produce no detectible hydro-peroxide. The amount of hydro-peroxide in a catalytic reaction mixture can be determined by methods known in the art. For example, the amount of hydro-peroxide can be determined by the use of quantitative electrochemical methods such as, for example, collection experiments,

performed with a rotating ring-disk electrode, or by the use of a scanning electrochemical microscope.

[0037] In an example, a method of oxidizing methanol, ethanol, formic acid, or other small organic molecules comprises contacting a CuPd composition (e.g., a thin film or nanoparticle) with methanol, ethanol, formic acid, or other small organic molecules (e.g., in gas form, liquid form, or in either form with an inert gas carrier or liquid carrier) under conditions such that at least part or all of the methanol, ethanol, formic acid, or other small organic molecules are oxidized to produce one or more oxidized product. The method may be carried out under alkaline conditions. The identification of suitable conditions for the oxidation is within the purview of one having skill in the art.

[0038] CuPd composition can function as catalysts under typical reaction conditions for reductions and oxidations in devices such as fuel cells, catalytic converters, industrial scrubbers, and electrolyzers.

[0039] In various examples, the oxidized product is substantially carbon dioxide. By “substantially” it is meant that 5 mol% or less of the products are oxidized products that are not carbon dioxide. In various examples, 1 mol% or less or 0.5 mol% or less of the products are oxidized products that are not carbon dioxide. In an example, there are no observable oxidized products that are not carbon dioxide. The amounts of oxidized products can be determined by methods known in the art. For example, amounts of oxidized products are determined by spectroscopic methods, mass spectrometric methods, chromatographic methods, or a combination thereof.

[0040] The CuPd compositions are stable under the catalytic reduction or catalytic oxidation reaction conditions of the present disclosure. By “stable” it is meant that the CuPd compositions do not substantially dealloy under the catalytic reduction or catalytic oxidation reaction conditions of the methods of the present disclosure. In various examples (e.g., palladium-rich and copper-rich compositions), the composition (Pd atom% and/or Cu atom%) of a CuPd composition does not change (e.g., loss of palladium atoms and/or copper atoms) by 5% or more, 4% or more, 3% or more, 2% or more, 1% or more, or 0.5% or more during the course of a catalytic reaction (e.g., initial Pd atom% and/or Cu atom% compared to Pd atom% and/or Cu atom% after the catalytic reaction).

[0041] In an aspect, the present disclosure provides a device comprising a CuPd composition. For example, the device is a catalytic converter, industrial scrubber, electrolyzer or fuel cell. An electrode (cathode and/or anode) of the device comprises a CuPd composition of the present disclosure.

[0042] In an example, the device is a fuel cell. The CuPd compositions may be used to catalyze the oxygen-reduction reaction in alkaline conditions, which can occur at the cathode of alkaline fuel cells. The CuPd film may also potentially be used in the anode of a fuel cell as well, depending on the type of fuel. One exemplary alkaline fuel cell is shown in FIG. 6. The CuPd film could be on both the cathode and anode of an alkaline fuel cell. For example, this may be an alkaline direct alcohol fuel cell (DAFC) employing methanol or ethanol as the material to be oxidized. While a particular alkaline fuel cell is illustrated in FIG. 6, other types of alkaline fuel cells can benefit from the use of a CuPd film on the cathode and/or anode. For example, a methanol pump, acidic/AEM fuel cell, or AEM direct methanol fuel cell can use this CuPd film as a catalyst on the cathode and/or anode.

[0043] In acid, as well as under alkaline conditions, CuPd is capable of oxidizing formic acid, methanol, ethanol, and borohydride, and may have catalytic activity for these reactions. A fuel cell can be assembled as such: in the anode, CuPd (or other compositions described above) nanoparticles supported on a material such as carbon black are deposited on the gas diffusion layer, with an alkaline exchange membrane ionomer. The alkaline exchange membrane can separate the cathode and the anode, and on the other side, in the cathode, there can be the same CuPd nanoparticles supported on a material such as carbon black and backed by the gas diffusion layer. Fuel cell systems can be constructed using methods known to those skilled in the art.

[0044] CuPd can also be used as an alkaline alcohol oxidation catalyst or for CO₂ reduction. These reactions also may occur in a fuel cell using the CuPd film as a catalyst on the anode and/or cathode.

[0045] The steps of the method described in the various embodiments and examples disclosed herein are sufficient to carry out the methods of the present disclosure. Thus, in an embodiment, a method consists essentially of a combination of the steps of the methods disclosed herein. In another embodiment, a method consists of such steps.

[0046] In the following Statements, various examples of the compositions, methods, and articles of manufacture of the present disclosure are described:

Statement 1. A CuPd thin film or nanoparticle comprising (or consisting essentially of or consisting of) 5 to 65 atom% Pd and 95 to 35 atom% Cu.

Statement 2. A CuPd thin film or nanoparticle according to Statement 1, wherein the CuPd thin film or nanoparticle comprises (or consists essentially of or consists of) 50 to 60 atom% Pd.

Statement 3. A CuPd thin film or nanoparticle according to any one or more of the preceding Statements, where the nanoparticle has a diameter of 1 to 50 nm.

Statement 4. A CuPd thin film or nanoparticle according to any one or more the preceding Statements, where the thin film has a thickness of 5 to 100 nm.

5 Statement 5. A CuPd thin film or nanoparticle according to any one or more of the preceding Statements, where the thin film or nanoparticle is a reduction catalyst (e.g., an alkaline, oxygen-reduction catalyst).

Statement 6. A CuPd thin film or nanoparticle according to any one or more of the preceding Statements, where the thin film or nanoparticle is an oxidation catalyst (e.g., a methanol
10 oxidation catalyst).

Statement 7. A CuPd thin film or nanoparticle according to any one or more of the preceding Statements, where the thin film or nanoparticle is disposed on a substrate (e.g., a planar or non-planar substrate).

Statement 8. A CuPd thin film or nanoparticle according to Statement 7, where the thin film
15 is disposed on an adhesive layer that is disposed on the substrate.

Statement 9. A CuPd thin film or nanoparticle according to any one or more of the preceding Statements, where the thin film or nanoparticle is a ternary composition (i.e., comprises, consists essentially of, or consists of a third metal).

Statement 10. A CuPd thin film or nanoparticle according to Statement 9, where the third
20 metal is Ag, Au, Ni, Co, Fe, or a combination thereof.

Statement 11. A device comprising one or more CuPd thin film or nanoparticle of the present disclosure (e.g., a CuPd thin film or nanoparticle according to any one or more of Statements 1 to 9).

Statement 12. A device according to Statement 11, where the device is a catalytic converter,
25 industrial scrubber, electrolyzer or fuel cell.

Statement 13. A device according to any of Statements 11 and/or 12, where the CuPd thin film or nanoparticle is one or more electrode (e.g., an oxygen and/or reduction catalyst such as, for example, an alkaline oxygen and/or reduction catalyst).

Statement 14. A fuel cell comprising: an anode; and a cathode, where the anode or the
30 cathode or both the anode and cathode independently comprises a CuPd thin film or nanoparticle of any of the preceding claims.

Statement 15. A fuel cell according to Statement 14, where the fuel cell is an alkaline fuel cell.

Statement 16. A fuel cell according to any of Statements 14 and/or 15, where the CuPd thin film or nanoparticle is an alkaline, oxygen-reduction catalyst.

Statement 17. A fuel cell according to any one or more of Statements 14 to 16, where the fuel cell is an alkaline direct alcohol fuel cell (DAFC).

5 Statement 18. A fuel cell according to any one or more of Statements 14 to 16, where the fuel cell comprises a methanol pump.

Statement 19. A fuel cell according to any one or more of Statements 14 to 16, where the fuel cell is an acidic/AEM fuel cell.

10 Statement 20. A fuel cell according to any one or more of Statements 14 to 16, where the fuel cell is an AEM direct methanol fuel cell.

Statement 21. A fuel cell according to any one or more of Statements 14 to 20, where the fuel cell is operated as an electrolyzer.

Statement 22. A fuel cell according to any one or more of Statements 14 to 21, where the fuel cell uses methanol, ethanol, hydrogen, formic acid, or borohydride as fuel.

15 Statement 23. A method of reducing or oxidizing oxygen, methanol, ethanol, carbon dioxide, hydrogen, formic acid, or borohydride comprising contacting a CuPd composition described herein (e.g., any one or more of Statements 1 to 9) with oxygen, methanol, ethanol, carbon dioxide, hydrogen, formic acid, or borohydride under conditions such that at least part or all of the oxygen, methanol, ethanol, carbon dioxide, hydrogen, formic acid, or borohydride is
20 reduced or oxidized.

Statement 24. A method according to Statement 23, where the method is carried out under alkaline conditions.

[0047] The following example is presented to illustrate the present disclosure. It is not intended to limiting in any manner.

25 **EXAMPLE 1**

[0048] This example provides a description of copper-palladium compositions of the present disclosure.

[0049] CuPd films were made by co-sputtering Cu and Pd onto glassy carbon substrates. First, a titanium adhesion (sticking) layer (12 nm thick) was sputtered in the same
30 chamber, and then Pd and Cu were simultaneously sputtered on top (50 nm thick CuPd layer). FIG. 1 shows a cross-sectional diagram of the film. Substrates were not heated during the deposition. The pressure during deposition was 5 mTorr of Ar.

[0050] After deposition, samples were removed and placed into a Pine Instruments exchangeable rotating disk electrode setup. Using this electrode holder, the samples were tested electrochemically to ascertain electrocatalytic activity (see FIG. 4 for a plot of the current density (current normalized to the plan view surface area of the film)). Compositions from 10-90 atom % Cu have been tested (see the FIG. 2), and compositions from 40 to 60 atom % Pd provide desirable results, both in terms of their activity and their cost. The Pd_{0.5}Cu_{0.5} composition (50 atom % Pd) has the benefit of high activity, and relatively lower cost, as shown in FIG. 3 (y-axis reduced to show trend better, but same data as previous graph without two of the points). By reducing the Pd to 40 atom %, most of the activity is retained (a 20 mV displacement in the onset potential) but the cost is reduced even further.

[0051] In one test, CuPd performed better than Pt or Pd. CuPd compositions with 50-60% Pd performed the best.

EXAMPLE 2

[0052] This example provides a description of copper-palladium compositions of the present disclosure.

[0053] Although there was a concern that very Cu-rich compositions would dissolve, further experiments doing X-ray photoelectron spectroscopy (XPS), which allows for analysis of the elemental composition of the surface, as well as the oxidation state (here only Cu was assessed), did not reveal that to be the case. The initial composition for Pd_{0.1}Cu_{0.9} (and Pd_{0.9}Cu_{0.1}) deviated from the target composition by about 15% (as a result of the films sitting for >1 month between deposition and analysis), but after electrochemical experimentation, the compositions in both actually matched the target, showing that Cu is not readily dissolving or corroding in these films. The Pd_{0.5}Cu_{0.5} composition also did not show evidence of Cu corrosion, instead showing a surface that was enriched in Cu after the experiment. The origin of this Cu-enrichment is unlikely to be Pd corrosion because of its greater stability, but may be caused by greater mobility of the Cu species. There could also be formation of a surface phase for which there is literature precedent.

[0054] Figure 7 provides structural data, showing that the compositions are all alloyed, as opposed to being an ordered intermetallic phase. Grazing incidence X-ray diffraction patterns (XRD) of Pd_{1-x}Cu_x compositions. XRD was performed on three 3" Si wafers, deposited with compositions of Pd_{0.5}Cu_{0.5}, Pd_{0.7}Cu_{0.3}, Pd_{0.3}Cu_{0.7} as the targeted composition. The continuous shifting peaks demonstrate that all phases are alloyed compositions as opposed to ordered intermetallics.

[0055] Table 1. Copper-palladium compositions before and after electrochemical experimentation.

	Pd _{0.9} Cu _{0.1}	Pd _{0.1} Cu _{0.9}	Pd _{0.5} Cu _{0.5}
Before	74% Pd, 26%Cu	27 % Pd, 73 % Cu	56 % Pd, 44 % Cu
	37% Cu ⁰ , 63 % CuO	58 % Cu ⁰ , 42 % CuO	64% Cu ⁰ , 36% CuO
After	92% Pd, 8% Cu	7% Pd, 93% Cu	15% Pd, 85% Cu
	62% Cu ⁰ , 38% CuO	15% Cu ⁰ , 85% CuO	88% Cu ⁰ , 12% CuO

What is claimed is:

1. A method of reducing or oxidizing oxygen, methanol, ethanol, carbon dioxide, hydrogen, formic acid, or borohydride comprising contacting a CuPd thin film or nanoparticle
- 5 comprising 5% to 65% Pd and 95% to 35% Cu with oxygen, methanol, ethanol, carbon dioxide, hydrogen, formic acid, or borohydride under conditions such that at least part or all of the oxygen, methanol, ethanol, carbon dioxide, hydrogen, formic acid, or borohydride is reduced or oxidized.
2. The method of claim 1, wherein the method is carried out under alkaline conditions.
- 10 3. The method of claim 1, wherein oxygen is contacted with the CuPd thin film or nanoparticle, the oxygen is reduced, and the method is carried out under alkaline conditions.
4. A CuPd thin film or nanoparticle comprising 5% to 65% Pd and 95% to 35% Cu.
5. The CuPd thin film or nanoparticle of claim 4, wherein the CuPd thin film or nanoparticle comprises 50% to 60% Pd.
- 15 6. The CuPd thin film or nanoparticle of claim 4, wherein the nanoparticle has a diameter of 1 nm to 50 nm.
7. The CuPd thin film or nanoparticle of claim 4, wherein the thin film has a thickness of 5 nm to 100 nm.
8. The CuPd thin film or nanoparticle of claim 4, wherein the thin film or nanoparticle is
- 20 disposed on a substrate.
9. The CuPd thin film or nanoparticle of claim 8, wherein the thin film is disposed on an adhesive layer that is disposed on the substrate.
10. The CuPd thin film or nanoparticle of claim 4, wherein the thin film or nanoparticle comprises a third metal.
- 25 11. The CuPd thin film or nanoparticle of claim 10, wherein the third metal is Ag, Au, Ni, Co, Fe, or a combination thereof.
12. A device comprising a CuPd thin film or nanoparticle of claim 4.

13. The device of claim 12, wherein the device is a catalytic converter, industrial scrubber, electrolyzer, or fuel cell.
14. The device of claim 12, wherein the device is a fuel cell and the fuel cell comprises:
an anode; and
5 a cathode,
wherein the anode or the cathode or both the anode and cathode independently comprises a CuPd thin film or nanoparticle of claim 4.
15. The fuel cell of claim 14, wherein the fuel cell is an alkaline fuel cell.
16. The fuel cell of claim 14, wherein the CuPd thin film or nanoparticle is an alkaline,
10 oxygen-reduction catalyst.
17. The fuel cell of claim 14, wherein the fuel cell is an alkaline direct alcohol fuel cell (DAFC).
18. The fuel cell of claim 14, wherein the fuel cell comprises a methanol pump.
19. The fuel cell of claim 14, wherein the fuel cell is an acidic/AEM fuel cell.
- 15 20. The fuel cell of claim 14, wherein the fuel cell is an AEM direct methanol fuel cell.
21. The fuel cell of claim 14, wherein the fuel cell is operated as an electrolyzer.
22. The fuel cell of claim 14, wherein the fuel cell uses methanol, ethanol, hydrogen, formic acid, or borohydride as fuel.

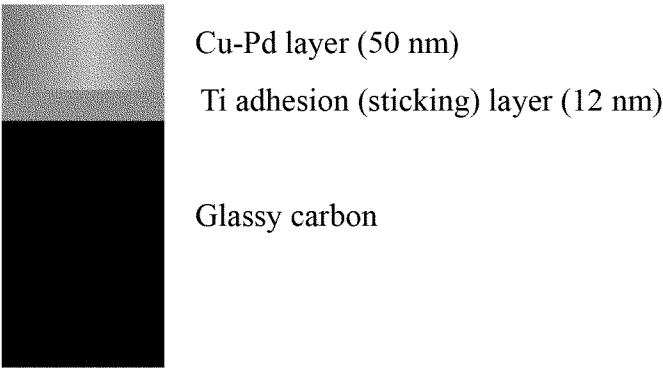


FIG. 1

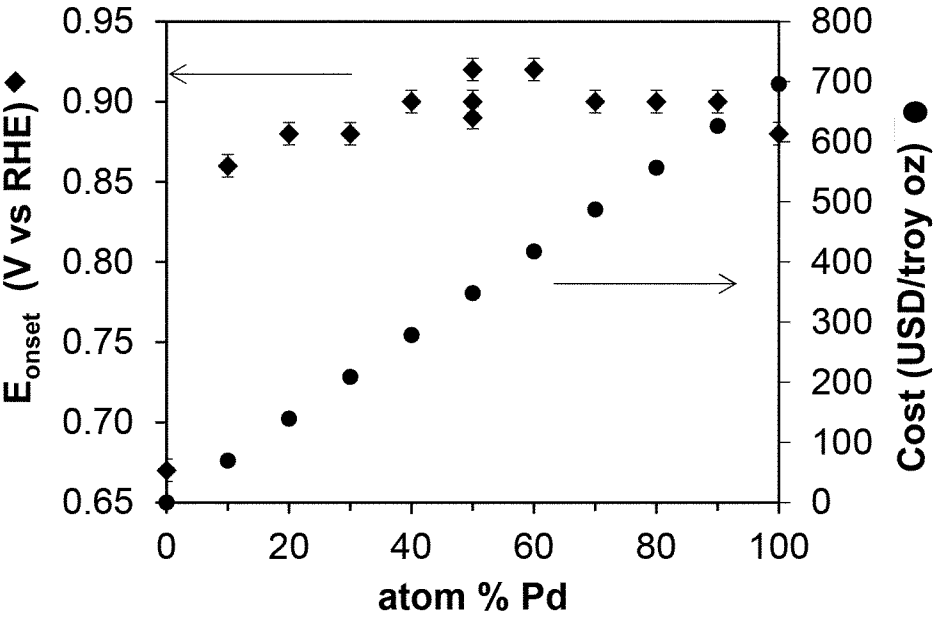


FIG. 2

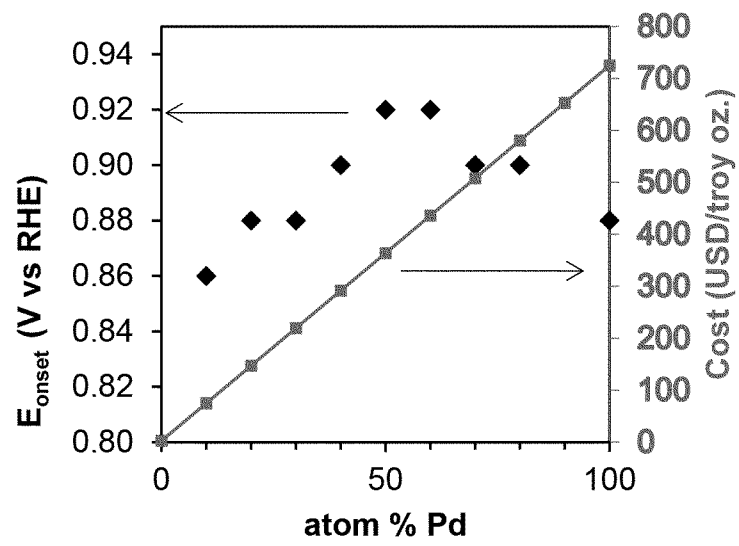


FIG. 3

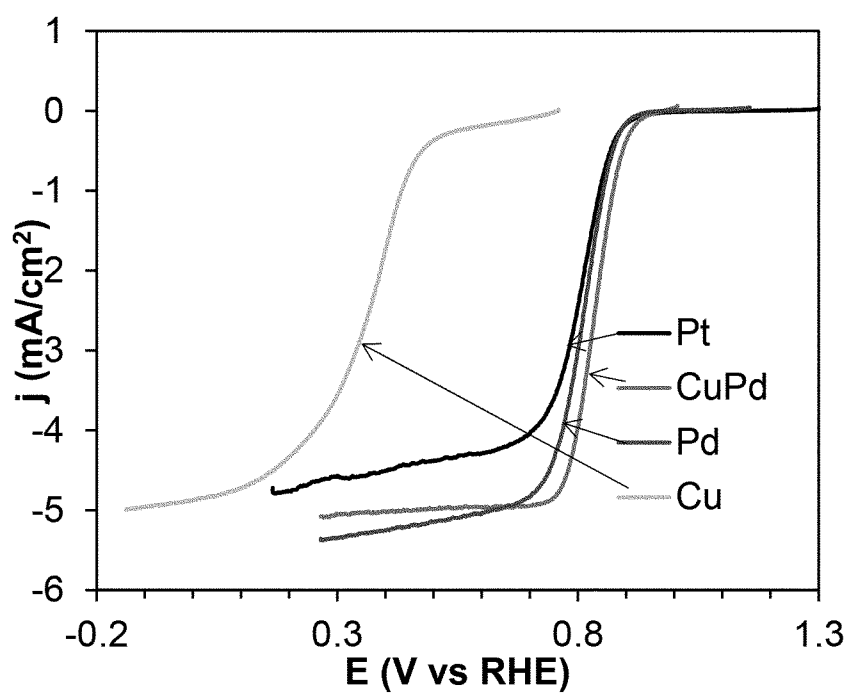


FIG. 4

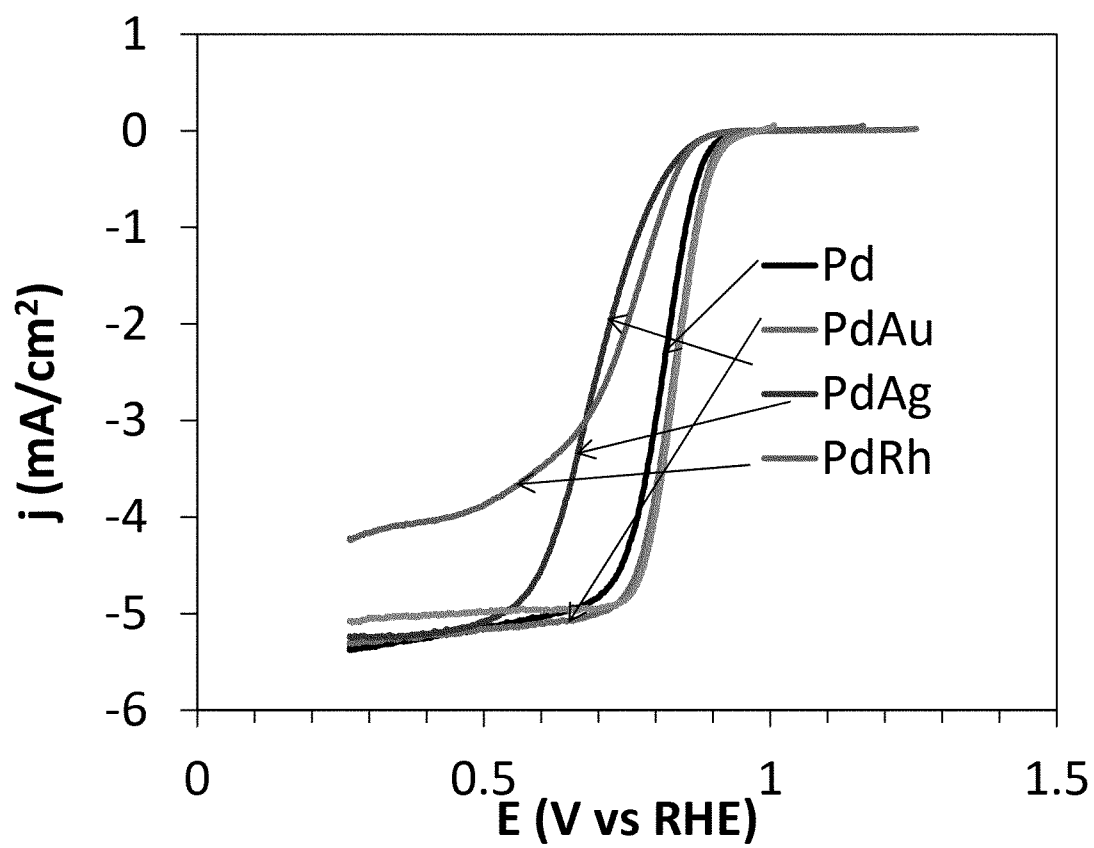


FIG. 5

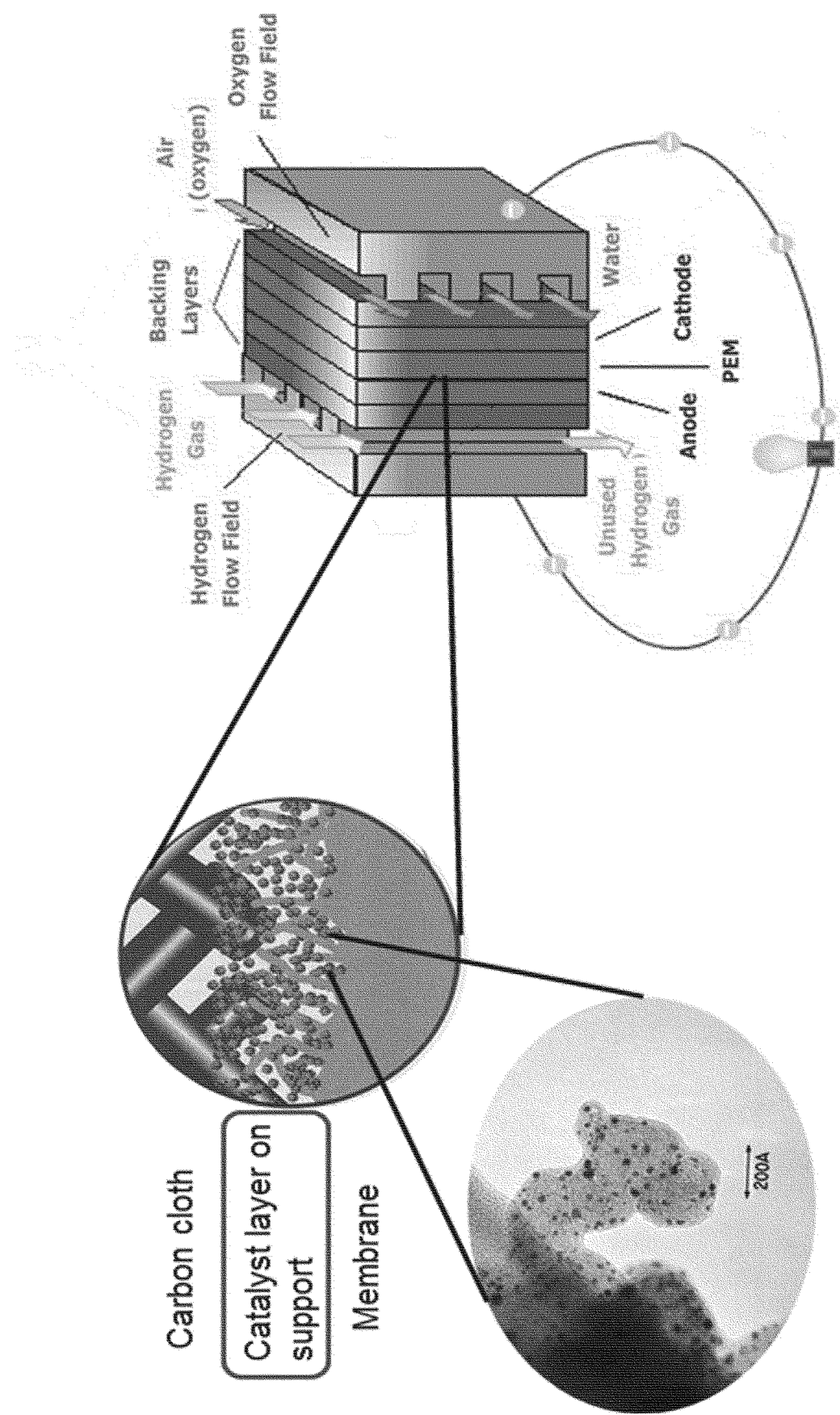


FIG. 6

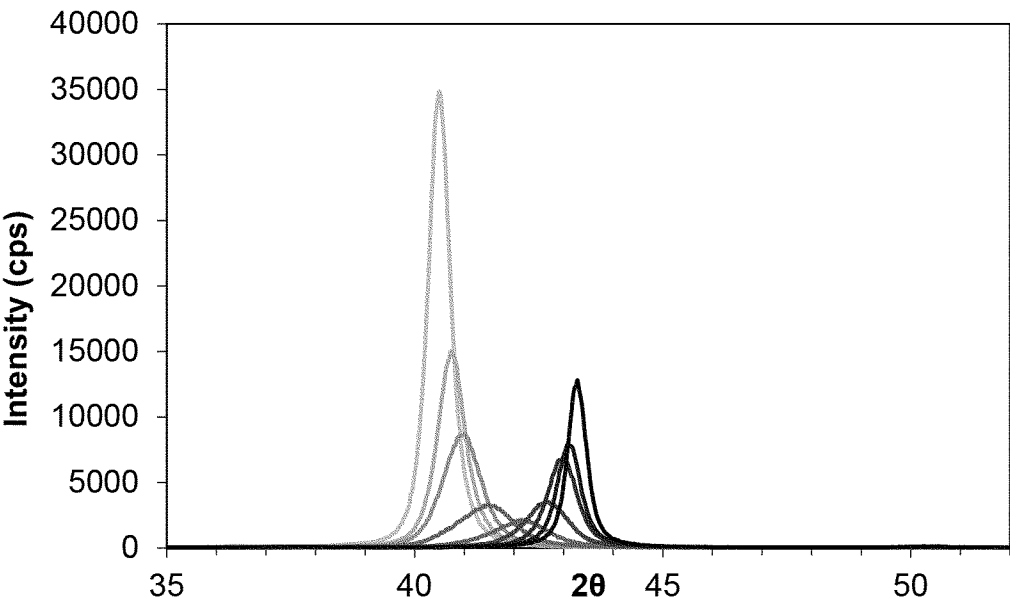


FIG. 7

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US16/42774

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01J 23/89; H01M 4/86, 4/92 (2016.01)

CPC - B01J 23/8926; H01M 4/86, 4/921

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)

IPC(8): B01J 23/00, 23/44, 23/72, 23/89; H01M 4/00, 4/86, 4/92, 4/94 (2016.01)

CPC: B01J 23/00, 23/44, 23/72, 23/89, 23/8926; H01M 4/00, 4/86, 4/8621, 4/8647, 4/92, 4/921, 4/926, 4/94

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)

PatSeer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, INPADOC Data); Google Scholar; EBSCO; IP.com; CuPd, PdCu, copper, palladium, nanoparticle, thin film, oxygen reduction, ORR, alkaline, fuel cell, thickness

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	(SHIH, ZY et al.) Porous palladium copper nanoparticles for the electrocatalytic oxidation of methanol in direct methanol fuel cells. Journal of Materials Chemistry A. March 2013. vol 1; abstract; pages 4773, 4775, 4777-4778	1-2, 4, 6, 12-13
X — Y	US 2009/0192030 A1 (MYERS, DJ et al.) 30 July 2009; paragraphs [0008]-[0012], [0046]; table II	1, 4-5, 8 — 3, 7, 9, 10-11
Y	(RAMASWAMY, N et al.) Fundamental Mechanistic Understanding of Electrocatalysis of Oxygen Reduction on Pt and Non-Pt Surfaces: Acid versus Alkaline Media. Advances in Physical Chemistry; 2012; abstract	3
Y	US 2014/0141600 A1 (SAMSUNG ELECTRONICS CO., LTD.) 22 May 2014; paragraph [0035]	7
Y	US 2004/0108205 A1 (LARSEN, LG) 10 June 2004; figure 1; paragraphs [0018]-[0019]	9
Y	US 4,745,094 A (BELLONI COFLER, J et al.) 17 May 1988; column 5, lines 56-65; column 7, lines 47-53	10-11

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

01 September 2016 (01.09.2016)

Date of mailing of the international search report

28 SEP 2016

Name and mailing address of the ISA/

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P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer

Shane Thomas

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US16/42774

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 14-22
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.