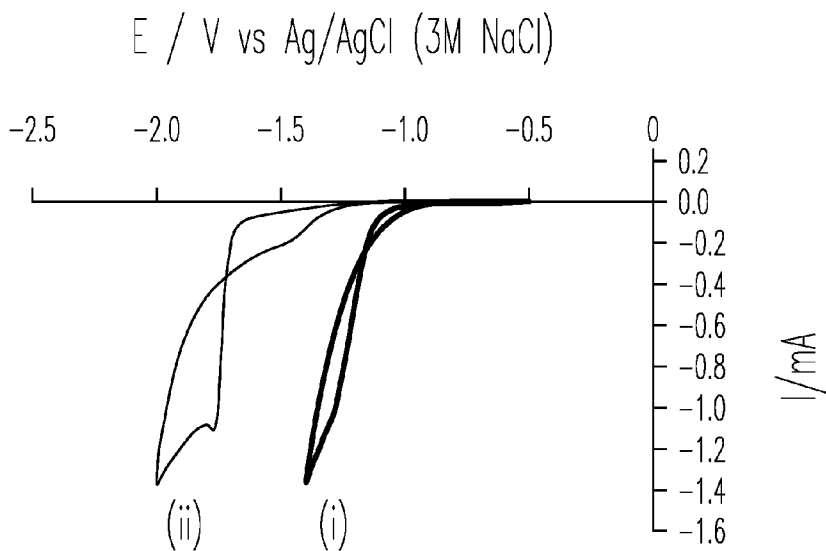




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(54) Title: ELECTROCHEMICAL DEPOSITION OF ELEMENTS IN AQUEOUS MEDIA



(57) **Abrégé/Abstract:**

The disclosure relates to a method for the electrodeposition of at least one metal onto a surface of a conductive substrate. In some embodiments, the electrodeposition is conducted at a temperature from about 10°C to about 70°C, about 0.5 atm to about 5 atm, in an atmosphere comprising oxygen. In some embodiments, the method comprises electrodepositing the at least one metal via electrochemical reduction of a metal complex dissolved in a substantially aqueous medium.

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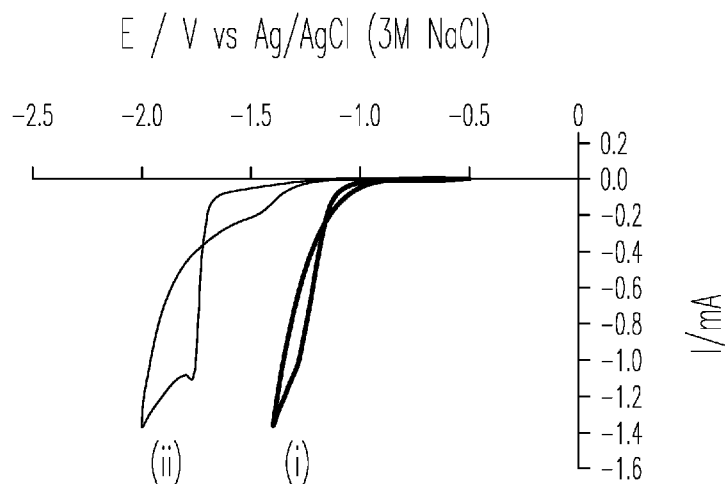


Fig. 2

(57) Abstract: The disclosure relates to a method for the electrodeposition of at least one metal onto a surface of a conductive substrate. In some embodiments, the electrodeposition is conducted at a temperature from about 10°C to about 70°C, about 0.5 atm to about 5 atm, in an atmosphere comprising oxygen. In some embodiments, the method comprises electrodepositing the at least one metal via electrochemical reduction of a metal complex dissolved in a substantially aqueous medium.

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ELECTROCHEMICAL DEPOSITION OF ELEMENTS IN AQUEOUS MEDIA

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BACKGROUND

[0001] Electrodeposition of metals, including aluminum, at ambient temperatures has been widely investigated owing to a variety of potential applications that include uses in corrosion-resistant applications, decorative coatings, performance coatings, surface aluminum alloys, electro-refining processes, and aluminum-ion batteries. Due to the large reduction potential of some metals, these materials have been exclusively used in non-aqueous media. For example, baths that have been developed for aluminum electrodeposition fall into three categories. These categories are inorganic molten salts, ionic liquids, and molecular organic solvents. Inorganic molten salt baths require a relatively high temperature (e.g., $>140^{\circ}\text{C}$). And in some instances, such baths are prone to the volatilization of corrosive gases. For example, AlCl_3 - NaCl - KCl baths suffer from the volatilization of corrosive AlCl_3 gas. In addition, baths that have been developed for aluminum electrodeposition have high energy consumption and material limitations of the substrate and apparatus.

[0002] Ionic liquid and organic solvent baths both allow electrodeposition of a metal, such as aluminum, at lower temperatures. For example, aluminum plating from room temperature ionic liquids has been the subject of a number of studies over the past few years. Still, an industrial process for aluminum electrodeposition from ionic liquids does not been realized, even though a manufacturing pilot plant was developed by Nisshin Steel Co., Ltd. The plant was not considered economically viable due to cost associated with materials and the need to perform plating in an inert atmosphere, free of humidity.

[0003] Commercial aluminum electroplating processes from organic solvents has been deployed with limited success. As of now, only two processes, namely, the Siemens Galvano Aluminium (SIGAL) process and Room-temperature Electroplated Aluminium (REAL) process have been deployed. The SIGAL process is currently licensed to AlumiPlate, Inc. and yields high quality aluminum. However,

organoaluminum processes are self-ignitable and extremely sensitive to atmospheric water.

SUMMARY

[0004] Disclosed herein is a method for the electrodeposition of at least one metal onto a surface of a conductive substrate. The electrodeposition is performed at a temperature from about 10°C to about 70°C and, in some instances, at a pressure of about 0.5 atm to about 5 atm, in an atmosphere comprising oxygen. The method of the various embodiments described herein comprises electrodepositing the at least one metal via electrochemical reduction of a metal complex dissolved in a substantially aqueous medium.

[0004-a] Another embodiment of the invention relates to a method for the electrodeposition of aluminum onto a surface of a conductive substrate at a temperature from 10°C to 70°C, 0.5 atm (50.66 kPa) to 5 atm (506.62 kPa), in an atmosphere comprising oxygen, the method comprising electrodepositing the aluminum via electrochemical reduction of an aluminum complex dissolved in an aqueous medium, the aluminum complex comprising an aluminum center and ligands; wherein the ligands are at least one of sulfonate ligands and sulfonimide ligands.

DESCRIPTION OF THE FIGURES

[0005] The drawings illustrate generally, by way of example, but not by way of limitation, various embodiments discussed in the present document.

[0006] FIG. 1 is a plot of a series for metal reductions versus that of proton reduction.

[0007] FIG. 2 is cyclic voltammograms for aluminum complexes at 1 M concentration in water (i) $\text{Al}(\text{Tf}_2\text{N})_3$; and (ii) AlCl_3 on a 3 mm glassy carbon working electrode vs. a Ag/AgCl (3M NaCl) reference electrode and an aluminum counter electrode and a 50 mVs^{-1} scan rate.

[0008] FIG. 3 is cyclic voltammograms for aluminum complexes in water (i) 6 M p-TSA; (ii) 0.5 M $\text{Al}(\text{p-TSA})_6$ (pH 0.24); (iii) 0.5 M $\text{Al}(\text{p-TSA})_4$; (iv) 0.5 M $\text{Al}(\text{p-TSA})_6$ with pH adjusted to 1.35 with NH_4OH ; and (v) 1 M AlCl_3 on a 3mm glassy carbon working electrode vs. a Ag/AgCl (3 M NaCl) reference electrode and an aluminum counter electrode and a 50 mVs^{-1} scan rate.

[0009] FIG. 4 is cyclic voltammograms for aluminum complexes in water (i) 1 M $\text{Al}(\text{MS})_3$ (pH 2.47); (ii) 3 M $\text{Al}(\text{MS})_3$ (pH 3.15); and (iii) 1 M AlCl_3 on a 3 mm glassy carbon working electrode vs. a Ag/AgCl (3 M NaCl) reference electrode and an aluminum counter electrode and a 50 mVs^{-1} scan rate.

[0010] FIG. 5 is a scanning electron microscopy (SEM)/ energy-dispersive X-ray (EDX) spectroscopy image of 20 AWG copper wire plated to a thickness in excess of $10 \mu\text{m}$ with aluminum.

DESCRIPTION

Introduction

[0011] Many commercially important elements from the periodic table cannot be easily electrodeposited from aqueous solutions because their reduction potentials can be much larger than the electrochemical window for water (e.g., the over-potential for the evolution of hydrogen gas due to water splitting). The various embodiments described herein provide an approach whereby the reduction potential of metals is “tuned” in a way that they are amenable to electrodeposition from aqueous solutions. In one embodiment, the reduction potential of the metal is tuned by selecting ligands that change the reduction potential of the metals such that the metal can be electrodeposited from an aqueous solution without, e.g., hydrogen gas generation. In other embodiments, the ligands are chosen in such a way that they affect the reduction potential of the metal center, thermodynamically, such that the reduction of the metal center occurs prior to the hydrogen evolution overpotential.

[0012] Some embodiments described herein, therefore, are directed to a method for the electrodeposition of at least one metal onto a surface of a conductive substrate. In some embodiments, the electrodeposition is conducted at a temperature from about 10°C to about 70°C (e.g., about 10°C to about 25°C ; about 10°C to about 40°C ; about 15°C to about 50°C ; about 25°C to about 50°C ; or about 30°C to about 50°C), about 0.5 atm to about 5 atm (e.g., about 0.5 atm to about 2 atm; 0.5 atm to about 1 atm; 1 atm to about 3 atm; 2 atm to about 5 atm or about 2 atm to about 3 atm), in an atmosphere comprising oxygen (e.g., in an atmosphere comprising about 1 to about 100% oxygen; about 5 to about 50% oxygen; about 10 to about 30% oxygen; about 15 to about 30% oxygen; about 20 to about 80% oxygen or about 25 to about 75% oxygen, the balance of the atmosphere

comprising gases including nitrogen, carbon dioxide, carbon monoxide, water vapor, etc.). In some embodiments, the method comprises electrodepositing the at least one metal via electrochemical reduction of a metal complex dissolved in a substantially aqueous medium. It should be understood that the method of the various embodiments described herein can also be conducted under conditions wherein the medium also contains at least some amount of dissolved oxygen (e.g., dissolved oxygen in the water present in the medium).

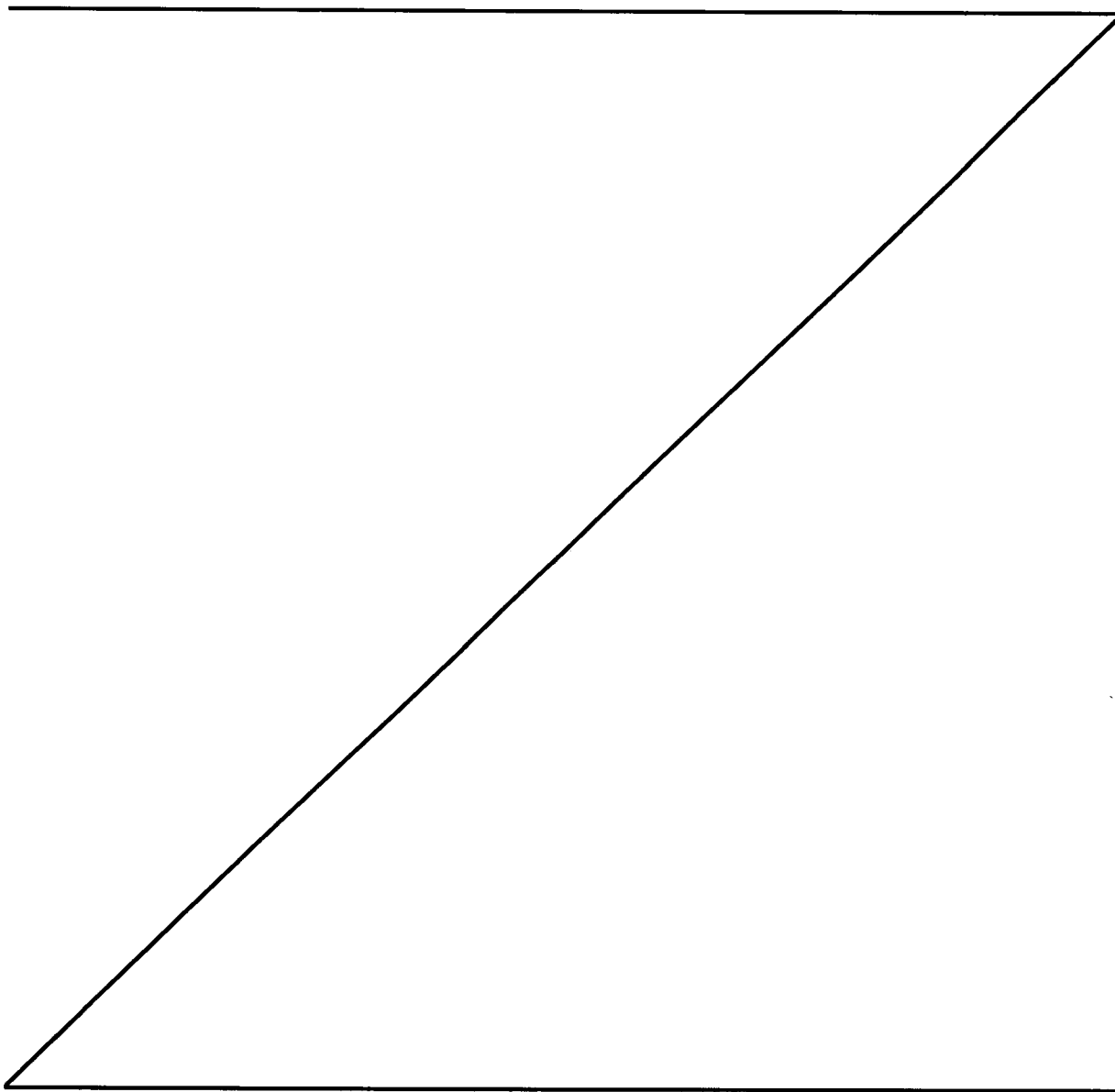
Metals

[0013] The metals that can be electrodeposited using the electrodeposition methods described herein are not limited. Electron withdrawing approach is applicable to at least the metals in Groups 2, 4, 5, 7, and 13. Metals useful in the methods described herein include metals having in general a Pauling electronegativity below 1.9 (e.g., about 1.3 to about 1.6; about 1.7 to about 1.9; and about 1.6 to about 1.9). Generally speaking, such metals would be considered nearly impossible to plate in water at high efficiency; or such metals would encounter problems with hydrogen embrittlement.

[0014] The electromotive series for the process $M^{n+} + ne^- \rightarrow M$, illustrated in FIG. 1 shows an example of a series for metal reductions versus that of proton reduction. Metals with a negative reduction are considered more difficult to reduce than protons in the presence of an acid source and are able to do so based on the high overpotential for proton reduction. These metals may have a reduced cathodic plating efficiency as a result of competitive hydronium ion reduction or an increased risk of hydrogen embrittlement. According to the various embodiments described herein, by addition of a suitable electron withdrawing ligand, any metal on this electromotive series may benefit from the reduction potential being made more positive by the inductive effect of the ligand thus creating a situation of increased efficiency for the plating process as compared with the hydrogen reduction overpotential. Examples of metals that are in the “electromotive series” include gold, platinum, iridium, palladium, silver, mercury, osmium, ruthenium, copper, bismuth, antimony, tungsten, lead, tin, molybdenum, nickel, cobalt, indium, cadmium, iron, chromium, zinc, niobium, manganese, vanadium, aluminum, beryllium, titanium, magnesium, calcium, strontium, barium, and potassium. See, e.g., EP0175901.

[0015] In some embodiments, suitable metals for use in the various methods described herein include metals that have a reduction potential from about 0 V to about -2.4 V.

[0016] In some embodiments, the metals that can be electrodeposited using the electrodeposition methods described herein can be “reactive” or “non-reactive” metals. The term “reactive,” as used herein, generally refers to metals that are reactive to, among other things, oxygen and water. Reactive metals include self-passivating metals. Self-passivating metals contain elements which can react



with oxygen to form surface oxides (e.g., such as the oxides of, but not limited to, Cr, Al, Ti, etc.). These surface oxide layers are relatively inert and prevent further corrosion of the underlying metal.

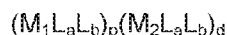
[0017] Examples of reactive metals include aluminum, titanium, manganese, gallium, vanadium, zinc, zirconium, and niobium. Examples of non-reactive metals include tin, gold, copper, silver, rhodium, and platinum.

[0018] Additional metals that can be electrodeposited using the electrodeposition methods described herein include molybdenum, tungsten, iridium, gallium, indium, strontium, scandium, yttrium, magnesium, manganese, chromium, lead, tin, nickel, cobalt, iron, zinc, niobium, vanadium, titanium, beryllium, and calcium.

Metal Complex

[0019] The metal complexes of the various embodiments described herein comprise a metal center and ligands associated with the metal center. In some embodiments, at least one of the ligands associated with the metal center is an electron withdrawing ligand.

[0020] Metal complexes of the various embodiments described herein include metal complexes of the formula:



wherein M_1 and M_2 each, independently represents a metal center; L is an electron withdrawing ligand; p is from 0 and 5; and d is from 0 and 5; a is from 1 to 8 (e.g., from 1 to 4; from 0.5 to 1.5; from 2 to 8; 2 to 6; and 4 to 6); and b is from 1 to 8 (e.g., from 1 to 4; from 0.5 to 1.5; from 2 to 8; 2 to 6; and 4 to 6). The metal complexes contemplated herein, therefore, can include metal complexes comprising more than one metal species and can even include up to ten different metal species when p and d are each 5. In addition, each of the metal complexes can have the same or different ligands around the metal center. Thus, for example, one can have two different metal complexes (e.g., when p is 1 and d is 1), the first being $Cr(SO_3R^1)_a$, and the second being $Mo(SO_3R^1)_a$. This combination of metal complexes can be used to electrodeposit a CrMo alloy on a surface of a substrate.

[0021] As used herein, the term "metal center" generally refers to a metal cation of a metal from Groups 2, 4, 5, 7, and 13. But it should be understood that

metal cations from Groups 2, 4, 5, 7, and 13 can be alloy plated using the methods described herein with metal cations from Groups 3, 6, 8, 9, 10, 11, and 12.

[0022] Some examples of "metal centers" include a cation of aluminum (e.g., Al^{+3}), titanium (e.g., Ti^{2+} , Ti^{3+} , and Ti^{+4}), manganese (e.g., Mn^{2+} and Mn^{3+}),
 5 gallium (e.g., Ga^{+3}), vanadium (e.g., V^{+2} , V^{3+} , and V^{+4}), zinc (e.g., Zn^{2+}), zirconium (e.g., Zr^{4+}), niobium (e.g., Nb^{+3} and Nb^{+5}), tin (e.g., Sn^{+2} and Sn^{+4}), gold (e.g., Au^{+1} and Au^{+3}), copper (e.g., Cu^{+1} and Cu^{+3}), silver (e.g., Ag^{+1}), rhodium (e.g., Rh^{+2} and Rh^{+4}), platinum (e.g., Pt^{+2} and Pt^{+4}), chromium (e.g., Cr^{+2} , Cr^{+3} , and Cr^{+6}), tungsten (e.g., W^{+4} and W^{+5}), and iridium (e.g., Ir^{+1} and Ir^{+4}).

10 **[0023]** As defined herein, the term "electron withdrawing ligand" generally refers to a ligand or combination of one or more (e.g., two to three; two to six; three to six; or four to six ligands) associated with the metal center, wherein the ligand or ligands are sufficiently electron withdrawing such that the reduction potential of the metal center in the metal complex is decreased below the over-potential for the
 15 evolution of hydrogen gas due to water splitting. The term "over-potential for the evolution of hydrogen gas due to water splitting" refers, in some instances, to a potential more negative than -1.4 V versus Ag/AgCl, where one generally observes significant hydrogen generation.

[0024] In some embodiments, electron withdrawing ligands can be ligands
 20 wherein the conjugate acid of the ligand has a pKa of from about 2 to about -5 (e.g., about -1.5 to about -4; about -2 to about -3; about -2 to about -4; about -1 to about -3; and about 2 to about -2).

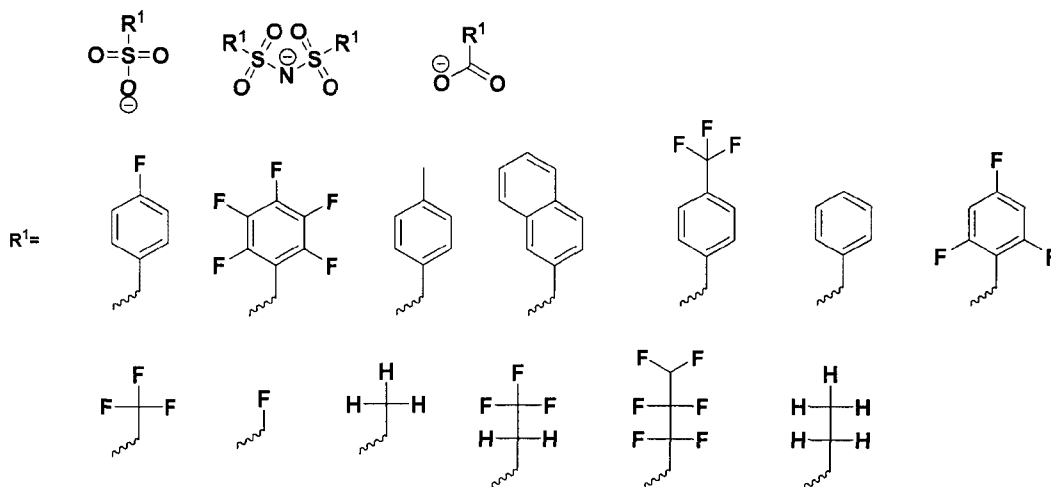
[0025] In some embodiments, the ligands that are useful in the methods described herein include sulfonate ligands, sulfonimide ligands, carboxylate
 25 ligands; and β -diketonate ligands.

[0026] Examples of sulfonate ligands include sulfonate ligands of the formula $^-\text{OSO}_2\text{R}^1$, wherein R^1 is halo; substituted or unsubstituted $\text{C}_6\text{-C}_{18}$ -aryl; substituted or unsubstituted $\text{C}_1\text{-C}_6$ -alkyl; substituted or unsubstituted $\text{C}_6\text{-C}_{18}$ -aryl- $\text{C}_1\text{-C}_6$ -alkyl.

30 **[0027]** Examples of sulfonimide ligands include ligands of the formula $^-\text{N}(\text{SO}_3\text{R}^1)$, wherein R^1 is wherein R^1 is halo; substituted or unsubstituted $\text{C}_6\text{-C}_{18}$ -aryl; substituted or unsubstituted $\text{C}_1\text{-C}_6$ -alkyl; substituted or unsubstituted $\text{C}_6\text{-C}_{18}$ -aryl- $\text{C}_1\text{-C}_6$ -alkyl.

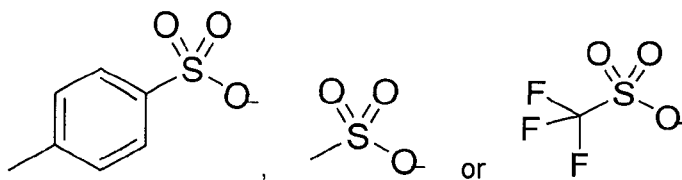
[0028] Examples of carboxylate ligands include ligands of the formula $R^1C(O)O^-$, wherein R^1 is halo; substituted or unsubstituted C_6 - C_{18} -aryl; substituted or unsubstituted C_1 - C_6 -alkyl; substituted or unsubstituted C_6 - C_{18} -aryl- C_1 - C_6 -alkyl. Other examples of carboxylate ligands include ligands of the formula $^-O(O)C-R^2-C(O)O^-$ wherein R^2 is (C_1-C_6) -alkylenyl or (C_3-C_6) -cycloalkylenyl.

[0029] In some embodiments, the ligands can be ligands such as the ones described in Scheme I, herein.

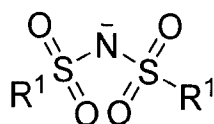


Scheme I

[0030] Specific examples of sulfonate ligands include sulfonate ligands of the formulae:

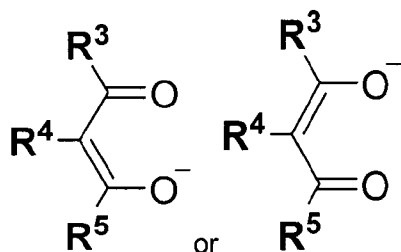


[0031] Specific examples of sulfonimide ligands include sulfonimide ligand of the formula:



wherein each R¹ is independently F or CF₃. In some embodiments, each R¹ is the same and can be F or CF₃.

[0032] Examples of β-diketonate ligands includes ligands of the formula:

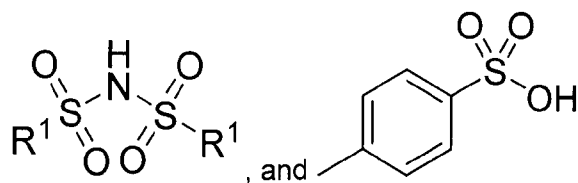


where R³, R⁴, and R⁵ may be substituted or unsubstituted C₆-C₁₈-aryl; substituted or unsubstituted C₁-C₆-alkyl; or substituted or unsubstituted C₆-C₁₈-aryl-C₁-C₆-alkyl, with the understanding that all resonance structures of the two β-diketonate ligands picture above, are also included.

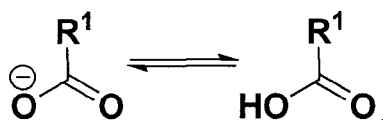
[0033] In some embodiments, α-diketonate ligands can have the formula R⁶C(=O)CHCHC(=O)R⁷, wherein R⁶ and R⁷ may be selected from alkoxy groups (e.g., methoxy, ethoxy, propoxy, hexyloxy octyloxy, and the like), aryloxy groups (e.g., phenoxy, biphenyloxy, anthracenyloxy, naphthyloxy, pyrenyloxy, and the like), and arylalkyloxy groups (e.g., benzyloxy, naphthyloxy, and the like).

[0034] In one embodiment, the ligand is acetylacetonate, also known as an “acac” ligand.

[0035] Some of the ligands described herein are shown in their deprotonated form (e.g., in the form of their conjugate base). Contemplated herein are also the ligands in their conjugate acid form such as, for example:



In addition, contemplated herein are ligands that can be in equilibrium between their conjugate acid and conjugate base forms, such as, for example:



[0036] Various ratios of metal to ligand are contemplated for use in the methods described herein. For example, the ratio of metal to ligand can be from about 1:50 to about 1:1 (e.g., from about 1:50 to about 1:25; about 1:30 to about 1:15; about 1:15 to about 1:5; about 1:10 to about 1:1; and about 1:10 to about 1:5).

[0037] The terms “halo,” “halogen,” or “halide” group, as used herein, by themselves or as part of another substituent, mean, unless otherwise stated, a fluorine, chlorine, bromine, or iodine atom.

[0038] The term “aryl,” as used herein, refers to substituted or unsubstituted cyclic aromatic hydrocarbons that do not contain heteroatoms in the ring. Thus aryl groups include, but are not limited to, phenyl, azulenyl, heptalenyl, biphenyl, indacenyl, fluorenyl, phenanthrenyl, triphenylenyl, pyrenyl, naphthacenyl, chrysenyl, biphenylenyl, anthracenyl, and naphthyl groups. In some embodiments, aryl groups contain about 6 to about 18 carbons (C₆-C₁₈; e.g., C₆-C₁₂; C₆-C₁₀; and C₁₂-C₁₈) in the ring portions of the groups. Representative substituted aryl groups can be mono-substituted or substituted more than once, such as, but not limited to, 2-, 3-, 4-, 5-, or 6-substituted phenyl or 2-8 substituted naphthyl groups.

[0039] The term “alkyl,” as used herein, refers to substituted or unsubstituted straight chain and branched alkyl groups and cycloalkyl groups having from 1 to 50 carbon atoms (C₁-C₅₀; e.g., C₁₀-C₃₀, C₁₂-C₁₈; C₁-C₂₀, C₁-C₁₀; C₁-C₈; C₁-C₆, and C₁-C₃). Examples of straight chain alkyl groups include those with from 1 to 8 carbon atoms (C₁-C₈) such as methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl groups. Examples of branched alkyl groups include, but are not limited to, isopropyl, iso-butyl, sec-butyl, t-butyl, neopentyl, isopentyl, 2,2-dimethylpropyl, and isostearyl groups. Examples of cycloalkyl groups include cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl groups.

[0040] The term “substituted” as used herein refers to a group (e.g., alkyl and aryl) or molecule in which one or more hydrogen atoms contained thereon are replaced by one or more “substituents.” The term “substituent” as used herein refers to a group that can be or is substituted onto a molecule or onto a group. Examples of substituents include, but are

not limited to, a halogen (e.g., F, Cl, Br, and I); an oxygen atom in groups such as hydroxyl groups, alkoxy groups, aryloxy groups, aralkyloxy groups, oxo(carbonyl) groups, carboxyl groups including carboxylic acids, carboxylates, and carboxylate esters; a sulfur atom in groups such as thiol groups, alkyl and aryl sulfide groups, sulfoxide groups, sulfone groups, sulfonyl groups, and sulfonamide groups; a nitrogen atom in groups such as amines, hydroxylamines, nitriles, nitro groups, N-oxides, hydrazides, azides, and enamines; and other heteroatoms in various other groups. Non-limiting examples of substituents that can be bonded to a substituted carbon (or other) atom include F, Cl, Br, I, OR, OC(O)N(R)₂, CN, NO, NO₂, ONO₂, azido, CF₃, OCF₃, R, O (oxo), S (thiono), C(O), S(O), methylenedioxy, ethylenedioxy, N(R)₂, SR, SOR, SO₂R, SO₂N(R)₂, SO₃R, C(O)R, C(O)C(O)R, C(O)CH₂C(O)R, C(S)R, C(O)OR, OC(O)R, C(O)N(R)₂, OC(O)N(R)₂, C(S)N(R)₂, (CH₂)₀₋₂N(R)C(O)R, (CH₂)₀₋₂N(R)N(R)₂, N(R)N(R)C(O)R, N(R)N(R)C(O)OR, N(R)N(R)CON(R)₂, N(R)SO₂R, N(R)SO₂N(R)₂, N(R)C(O)OR, N(R)C(O)R, N(R)C(S)R, N(R)C(O)N(R)₂, N(R)C(S)N(R)₂, N(COR)COR, N(OR)R, C(=NH)N(R)₂, C(O)N(OR)R, or C(=NOR)R, wherein R can be, for example, hydrogen, alkyl, acyl, cycloalkyl, aryl, aralkyl, heterocyclyl, heteroaryl, or heteroarylalkyl.

[0041] The term “acyl” as used herein refers to a group containing a carbonyl moiety wherein the group is bonded via the carbonyl carbon atom. The carbonyl carbon atom is also bonded to another carbon atom, which can be part of a substituted or unsubstituted alkyl, aryl, aralkyl, cycloalkyl, cycloalkylalkyl, heterocyclyl, heterocyclylalkyl, heteroaryl, heteroarylalkyl group or the like. In the special case wherein the carbonyl carbon atom is bonded to a hydrogen, the group is a “formyl” group, an acyl group as the term is defined herein. An acyl group can include 0 to about 12-40, 6-10, 1-5 or 2-5 additional carbon atoms bonded to the carbonyl group. An acryloyl group is an example of an acyl group. An acyl group can also include heteroatoms within the meaning here. A nicotinoyl group (pyridyl-3-carbonyl) is an example of an acyl group within the meaning herein. Other examples include acetyl, benzoyl, phenylacetyl, pyridylacetyl, cinnamoyl, and acryloyl groups and the like. When the group containing the carbon atom that is bonded to the carbonyl carbon atom contains a halogen, the group is termed a “haloacyl” group. An example is a trifluoroacetyl group.

[0042] The term “aralkyl,” “arylalkyl,” and “aryl-alkyl” as used herein refers to alkyl groups as defined herein in which a hydrogen or carbon bond of an alkyl group is replaced with a bond to an aryl group as defined herein. Representative aralkyl groups include benzyl and phenylethyl groups.

[0043] The term “heteroaralkyl” and “heteroarylalkyl” as used herein refers to alkyl groups as defined herein in which a hydrogen or carbon bond of an alkyl group is replaced with a bond to a heteroaryl group as defined herein.

[0044] The term “heterocyclyl” as used herein refers to substituted or unsubstituted aromatic and non-aromatic ring compounds containing 3 or more ring members, of which, one or more is a heteroatom such as, but not limited to, N, O, and S. Thus, a heterocyclyl can be a cycloheteroalkyl, or a heteroaryl, or if polycyclic, any combination thereof. In some embodiments, heterocyclyl groups include 3 to about 20 ring members, whereas other such groups have 3 to about 15 ring members. In some embodiments, heterocyclyl groups include heterocyclyl groups that include 3 to 8 carbon atoms (C₃-C₈), 3 to 6 carbon atoms (C₃-C₆) or 6 to 8 carbon atoms (C₆-C₈). A heterocyclyl group designated as a C₂-heterocyclyl can be a 5-ring with two carbon atoms and three heteroatoms, a 6-ring with two carbon atoms and four heteroatoms and so forth. Likewise a C₄-heterocyclyl can be a 5-ring with one heteroatom, a 6-ring with two heteroatoms, and so forth. The number of carbon atoms plus the number of heteroatoms equals the total number of ring atoms. A heterocyclyl ring can also include one or more double bonds. A heteroaryl ring is an embodiment of a heterocyclyl group. The phrase “heterocyclyl group” includes fused ring species including those that include fused aromatic and non-aromatic groups. Representative heterocyclyl groups include, but are not limited to piperidynyl, piperazinyl, morpholinyl, furanyl, pyrrolidinyl, pyridinyl, pyrazinyl, pyrimidinyl, triazinyl, thiophenyl, tetrahydrofuranyl, pyrrolyl, oxazolyl, imidazolyl, triazyolyl, tetrazolyl, benzoxazolynyl, and benzimidazolynyl groups.

[0045] The term “alkoxy” as used herein refers to an oxygen atom connected to an alkyl group, including a cycloalkyl group, as are defined herein. Examples of linear alkoxy groups include but are not limited to methoxy, ethoxy, propoxy, butoxy, pentyloxy, hexyloxy, and the like. Examples of branched alkoxy include but are not limited to isopropoxy, sec-butoxy, tert-butoxy, isopentyloxy, isohexyloxy, and the like. Examples of cyclic alkoxy

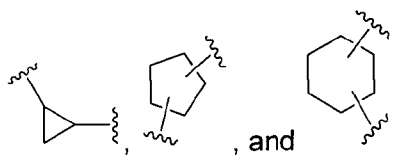
include but are not limited to cyclopropyloxy, cyclobutyloxy, cyclopentyloxy, cyclohexyloxy, and the like. An alkoxy group can include one to about 12-20 or about 12-40 carbon atoms bonded to the oxygen atom, and can further include double or triple bonds, and can also include heteroatoms. For example, an allyloxy group is an alkoxy group within the meaning herein. A methoxyethoxy group is also an alkoxy group within the meaning herein, as is a methylenedioxy group in a context where two adjacent atoms of a structure are substituted therewith.

[0046] The term “aryloxy” and “heteroaryloxy” as used herein refers to an oxygen atom connected to an aryl group or a heteroaryl group, as the terms are defined herein. Examples of aryloxy groups include but are not limited to phenoxy, naphthyloxy, and the like. Examples of heteroaryloxy groups include but are not limited to pyridoxy and the like.

[0047] The term “amine” as used herein refers to primary, secondary, and tertiary amines having, e.g., the formula $N(\text{group})_3$ wherein each group can independently be H or non-H, such as alkyl, aryl, and the like. Amines include but are not limited to alkylamines, arylamines, arylalkylamines; dialkylamines, diarylamines, diaralkylamines, heterocyclylamines and the like; and ammonium ions.

[0048] The term “alkylenyl” as used herein refers to straight chain and branched, saturated divalent groups having from 1 to 20 carbon atoms, 10 to 20 carbon atoms, 12 to 18 carbon atoms, 1 to about 20 carbon atoms, 1 to 10 carbons, 1 to 8 carbon atoms or 1 to 6 carbon atoms. Examples of straight chain alkylenyl groups include those with from 1 to 6 carbon atoms such as $-\text{CH}_2-$, $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$, and $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$. Examples of branched alkylenyl groups include $-\text{CH}(\text{CH}_3)\text{CH}_2-$ and $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2-$.

[0049] The term “cycloalkylenyl” as used herein refers to cyclic (mono- and polycyclic, including fused and non-fused polycyclic), saturated carbon-only divalent groups having from 3 to 20 carbon atoms, 10 to 20 carbon atoms, 12 to 18 carbon atoms, 3 to about 10 carbon atoms, 1 to 10 carbons, 1 to 8 carbon atoms or 1 to 6 carbon atoms. Examples of cycloalkylenyl groups include:



wherein the wavy lines represent the points of attachment to, e.g., the moieties -C(O)O^- .

[0050] In some embodiments, the metal complex is at least one metal complex of the formula $\text{Al}(\text{SO}_3\text{R}^1)_n$, wherein R^1 is halo; substituted or unsubstituted $\text{C}_6\text{-C}_{18}\text{-aryl}$; substituted or unsubstituted $\text{C}_1\text{-C}_6\text{-alkyl}$; substituted or unsubstituted $\text{C}_6\text{-C}_{18}\text{-aryl-C}_1\text{-C}_6\text{-alkyl}$; n is an integer from 2 to 8; and $\text{Al}[\text{N}(\text{SO}_3\text{R}^1)_2]_n$, wherein R^1 is halo; substituted or unsubstituted $\text{C}_6\text{-C}_{18}\text{-aryl}$; substituted or unsubstituted $\text{C}_1\text{-C}_6\text{-alkyl}$; substituted or unsubstituted $\text{C}_6\text{-C}_{18}\text{-aryl-C}_1\text{-C}_6\text{-alkyl}$; and n is an integer from 1 to 4.

[0051] Although not wishing to be bound by any specific theory, it is believed that the metal complex can be additionally complexed with any species present in the substantially aqueous medium that is capable of complexing with the metal center. For example, in some instances, the substantially aqueous medium is buffered with a citrate buffer. It is possible that the metal center of the metal complex can coordinate not only with electron withdrawing ligands, but also with the citrate in the buffer.

Substantially Aqueous Medium

[0052] The various embodiments of the methods described herein comprise electrodepositing the at least one metal via electrochemical reduction of a metal complex dissolved in a substantially aqueous medium.

[0053] In some embodiments, the substantially aqueous medium comprises an electrolyte. Generally speaking, the electrolyte can comprise any cationic species coupled with a corresponding anionic counterion (e.g., some of the sulfonate ligands, sulfonimide ligands, carboxylate ligands; and β -diketonate ligands described herein). Cationic species include, for example, a sulfonium cation, an ammonium cation, a phosphonium cation, a pyridinium cation, a bipyridinium cation, an amino pyridinium cation, a pyridazinium cation, an oxazolium cation, a pyrazolium cation, an imidazolium cation, a pyrimidinium cation, a triazolium cation, a thiazolium cation, an acridinium cation, a quinolinium cation, an

isoquinolinium cation, an orange-acridinium cation, a benzotriazolium cation, or a methimzolium cation. See, e.g., Published U.S. Appl. No. 2013/0310569.

[0054] An electrolyte can also comprise a cationic metal with a more negative reduction potential than the metal center in the metal complex of the various embodiments described herein. In other embodiments, the electrolyte can comprise any suitable cation, including $^+NR_4$, wherein each R is independently hydrogen or C₁-C₆-alkyl; $^+PR_4$, wherein each R is independently hydrogen or C₁-C₆-alkyl; imidazolium, pyridinium, pyrrolidinium, piperadinium; and $^+SR_3$; in combination with any suitable anion.

[0055] Examples of electrolytes include electrolytes comprising at least one of a halide electrolyte (e.g., tetrabutylammonium chloride, bromide, and iodide); a perchlorate electrolyte (e.g., lithium perchlorate, sodium perchlorate, and ammonium perchlorate); an amidosulfonate electrolyte; hexafluorosilicate electrolyte (e.g., hexafluorosilicic acid); a tetrafluoroborate electrolyte (e.g., tetrabutylammonium tetrafluoroborate); a sulfonate electrolyte (e.g., tin methanesulfonate); and a carboxylate electrolyte.

[0056] Examples of carboxylate electrolytes include electrolytes comprising at least one of compound of the formula $R^3CO_2^-$, wherein R^3 is substituted or unsubstituted C₆-C₁₈-aryl; substituted or unsubstituted C₁-C₆-alkyl. Carboxylate electrolytes also include polycarboxylates such as citrate (e.g., sodium citrate); and lactones, such as ascorbate (e.g., sodium ascorbate).

[0057] But in some embodiments, the metal complex can also act as an electrolyte.

[0058] In sum, it should be understood that: (i) the metal complex can be the electrolyte (e.g., have a dual function as metal complex for electrodeposition and as electrolyte); (ii) when a buffer is used, the metal complex, in combination with the buffer, can be the electrolyte; (iii) the metal complex, in combination with a non-buffering electrolyte, can be the electrolyte; or (iv) the metal complex, in combination with a non-buffering electrolyte and an additional non-buffering salt (e.g., sodium chloride and potassium chloride), can be the electrolyte.

[0059] In some embodiments the substantially aqueous medium has a pH of from about 1 to about 7 (e.g., about 2 to about 4; about 3 to about 6; about 2 to about 5; about 3 to about 7; or about 4 to about 7). In other embodiments, the substantially aqueous medium

is buffered at a pH of between about 1 and about 7 (e.g., about 2 to about 4; about 3 to about 6; about 2 to about 5; about 3 to about 7; or about 4 to about 7) using an appropriate buffer.

[0060] In some embodiments, the substantially aqueous medium comprises a water-miscible organic solvent. The water-miscible organic solvent comprises at least one of an C₁-C₆-alkanol (ethanol, methanol, 1-propanol, and 2-propanol); a C₂-C₁₀-polyol (e.g., 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,3-propanediol, 1,5-propanediol, ethylene glycol, propylene glycol, diethylene glycol, and glycerol); a (poly)alkylene glycol ether (e.g., glyme and diglyme); a C₂-C₁₀-carboxylic acid (e.g., ethanoic acid, acetic acid, butyric acid, and propanoic acid); a C₂-C₁₀-ketone (e.g., acetone, 2-butanone, cyclohexanone, and acetylacetone); a C₂-C₁₀-aldehyde (e.g., acetaldehyde); a pyrrolidone (e.g., N-Methyl-2-pyrrolidone); a C₂-C₁₀-nitrile (e.g., acetonitrile); a phthalate (e.g., di-n-butylphthalate); a C₂-C₁₀-dialkylamine (e.g., diethylamine); a C₂-C₁₀-dialkylformamide (e.g., dimethylformamide); a C₂-C₁₀-dialkyl sulfoxide (dimethyl sulfoxide); a C₄-C₁₀-heterocycloalkane (e.g., dioxane and tetrahydrofuran); aminoalcohols (e.g., aminoethanol); and a C₄-C₁₀-heteroarylene (e.g., pyridine).

Substrate

[0061] Embodiments described herein are directed to a method for the electrodeposition of at least one metal onto a surface of a conductive substrate.

[0062] As defined herein, the term “substrate” includes any material with a resistivity of less than 1 Ωm (at 20°C). Some metallic substrates will naturally have such a resistivity. But the requisite resistivity can be achieved for non-metallic substrates by methods known in the art. For example, through doping, as is the case for semi-conductors comprising primarily of silicon; or by pretreatment of the substrate with an alternative coating technique to deposit a thin, adherent layer with a surface resistivity of less than 1 Ωm, as is the case for plastics, precoated with a metal such as copper.

[0063] Other substrates include, for example, plastics that are doped with a carbon material (e.g., carbon nanotubes and graphene) to the point where they are suitably conductive; and electron conductive polymers such as polypyrrole and polythiophene.

Applications

[0064] In some embodiments, the methods described herein can be used to electrodeposit at least one layer (e.g., at least two) of the at least one (e.g., at least two) metal onto a surface of a substrate. In some embodiments, each layer can comprise one or more different metals. In other embodiments, when there are at least two layers that are electrodeposited, a first layer comprises different at least one metal relative to the second layer.

[0065] The electrodeposition methods described herein can therefore be used to in a variety of different applications, including: electrodesposition of corroding resistant alloys; generating biomedical coatings; generating automotive coatings; generating catalysis coatings; growing refractory material over metallic substrates (e.g., materials used in kilns, power plants, glass smelters, steel manufacturing, etc., which would have use for growing refractory materials on an aluminum oxide layer to generate a ceramic coating with a metal backing); thermal barrier coatings for, e.g., gas turbines; water infrastructure coatings, to imbue the infrastructure with, among other things, resistance to sulfates, alkaline conditions, and improved corrosion resistance towards hot water; highway and aerospace infrastructure, to imbue the infrastructure with improved corrosion against natural elements, salts, and de-icing fluids); nano-patterning and applications in electronics and lithography; generating metal alloys; improve adhesion of, e.g., paint to a surface by creating hydroxylic functionality on aluminum oxide layers; electro-coat applications where, for example sharp edges on a metal surface are first coated with a second metal and the coated metal is subsequently cationic epoxy electrocoated); creating non-adhesives substrates by co-depositing nickel-Teflon® on a substrate; generating primer coatings for e-coat applications, as well as aerospace and automotive coatings; applications in galvanic corrosions, where dissimilar metals may be in contact; metal purification; optics and radiator absorbers; light to thermal conversion devices; heat exchangers; creating coatings comprising nano- or microparticles of diamond, Teflon®, carbon black, talc, where the nano- or microparticles are suspended in the substantially aqueous medium and they would be included in the plating.

[0066] The term “about” as used herein can allow for a degree of variability in a value or range, for example, within 10%, within 5%, or within 1% of a stated value or of a stated limit of a range.

[0067] The term “substantially” as used herein refers to a majority of, or mostly, as in at least about 50%, 60%, 70%, 80%, 90%, 95%, 96%, 97%, 98%, 99%, 99.5%, 99.9%, 99.99%, or at least about 99.999% or more.

[0068] Values expressed in a range format should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range were explicitly recited. For example, a range of “about 0.1% to about 5%” or “about 0.1% to 5%” should be interpreted to include not just about 0.1% to about 5%, but also the individual values (e.g., 1%, 2%, 3%, and 4%) and the sub-ranges (e.g., 0.1% to 0.5%, 1.1% to 2.2%, 3.3% to 4.4%) within the indicated range. The statement “about X to Y” has the same meaning as “about X to about Y,” unless indicated otherwise. Likewise, the statement “about X, Y, or about Z” has the same meaning as “about X, about Y, or about Z,” unless indicated otherwise.

[0069] In this document, the terms “a,” “an,” or “the” are used to include one or more than one unless the context clearly dictates otherwise. The term “or” is used to refer to a nonexclusive “or” unless otherwise indicated. In addition, it is to be understood that the phraseology or terminology employed herein, and not otherwise defined, is for the purpose of description only and not of limitation. Any use of section headings is intended to aid reading of the document and is not to be interpreted as limiting. Further, information that is relevant to a section heading may occur within or outside of that particular section.

[0070] In the methods described herein, the steps can be carried out in any order without departing from the principles of the invention, except when a temporal or operational sequence is explicitly recited. Furthermore, specified steps can be carried out concurrently unless explicit claim language recites that they be carried out separately. For example, a claimed step of doing X and a claimed step of doing Y can be conducted simultaneously within a single operation, and the resulting process will fall within the literal scope of the claimed process.

EXAMPLES

[0071] The examples described herein are intended solely to be illustrative, rather than predictive, and variations in the manufacturing and testing procedures can yield different results. All quantitative values in the Examples section are understood to be approximate in view of the commonly known tolerances involved in the procedures used. The foregoing detailed description and examples have been given for clarity of understanding only. No unnecessary limitations are to be understood therefrom.

Materials

[0072] Aluminum carbonate ($\text{Al}_2(\text{CO}_3)_3$, Alfa Aesar); aluminum chloride (AlCl_3 , anhydrous, $\geq 98.0\%$, TCI); bis(trifluoromethane)sulfonamide (Tf_2NH , $\geq 95.0\%$, Sigma-Aldrich); methanesulfonic acid (MsOH , 99%, Acros Organics); *p*-toluenesulphonic acid (TsOH , monohydrate, 98.5+%, Alfa Aesar); trifluoromethanesulfonic acid (TfOH , 99%, Oakwood Chemical); trifluoroacetic acid (TFA, 99%, Alfa Aesar); polyvinyl alcohol (PVA, average M_w 13000-23000, 98% hydrolyzed, Sigma-Aldrich); ammonium acetate ($\text{CH}_3\text{CO}_2\text{NH}_4$, 97%, Alfa Aesar); ammonium hydroxide solution (NH_4OH , ACS reagent, Sigma-Aldrich); and citric acid (97%, Alfa Aesar) were used without further purification.

Example 1: Synthesis of 1 M $\text{Al}(\text{NTf}_2\text{N})_3$ aqueous solution

[0073] To a mixture of $\text{Al}_2(\text{CO}_3)_3$ (138 g, 0.59 mol, 1 eq) in H_2O (600 mL), HTf_2N aqueous solution (6 eq., 995 g, 3.54 mol; in 300 mL H_2O) was added portion-wise under magnetic stirring at room temperature. The turbid mixture foamed and became warm. After 2 h, the mixture was heated at 60°C overnight and afforded a transparent light yellow liquid. After the mixture was cooled down to room temperature, additional H_2O was added to make the total volume of the mixture 1.2 L.

Example 2: General procedures for preparation aluminum complex aqueous solutions for cyclic voltammetry (CV) experiments

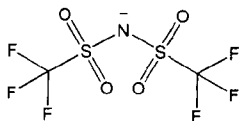
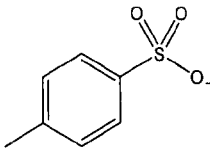
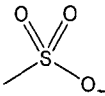
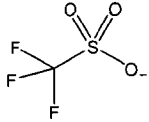
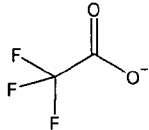
[0074] To prepare 2 mL aluminum complex aqueous solutions, a mixture of $\text{Al}_2(\text{CO}_3)_3$ (0.23 g, 1 mmol) and H_2O (0.5 mL) was stirred at room temperature. Organic acid (6 or 12 mmol; 3 or 6 eq. to Al, see Table 1) was added slowly into the mixture and yielded a turbid aqueous mixture. After stirring for another 1 hour, the mixture was heated to approximately 60°C overnight and give a clear liquid. After the mixture was cooled to room

temperature, H₂O was added to adjust the solution to certain molarity (0.5 or 1 M, see Table 1).

Table 1

Compound	Compound abbreviation	Organic acid used in synthesis	(ligand) to Al ratio	Aluminum Molarity / M	pH	Reduction onset potential / V
Aluminum chloride	AlCl ₃	N/A	3:1	1	2.04	-1.67
Aluminum bis(trifluoromethane) sulfonimide	Al(Tf ₂ N) ₃	Tf ₂ NH	3:1	1	1.91	-1.10
	Al(Tf ₂ N) ₁		1:1	1	3.30	-1.20
Aluminum methanesulfonate	Al(MS) ₃	MsOH	3:1	1	2.47	-0.84
	Al(MS) ₆		6:1	1	1.00	-1.11
	Al(MS) ₁		1:1	3	3.15	-1.12
Aluminum <i>p</i> -toluenesulphonate	Al(OTs) ₃	TsOH	3:1	1	2.36	-1.13
	Al(OTs) ₆		6:1	0.5	0.24	-0.93
	Al(OTs) ₆		6:1	0.5	1.35	-1.17
Aluminum trifluoromethanesulfonate	Al(OTf) ₆	TfOH	6:1	1	2.82	-1.35
Aluminum trifluoroacetate	Al(TFA) ₃	TFA	3:1	0.5	3.17	-1.10
	Al(TFA) ₆		6:1	0.5	0.78	only gas evolution
	Al(TFA) ₆		6:1	0.5	1.18	-1.07
	Al(TFA) ₆		6:1	0.5	3.34	-1.32

Table 2

Ligand	Structure	pKa in water
bis(trifluoromethane)sulfonamide (Tf ₂ N)		Too negative to measure
p-Toluenesulfonate (p-TSA)		-2.14
Methanesulfonate (MSO)		-1.61
Triflate (TfO)		-3.43
Trifluoroacetate (TFA)		0.52

Example 3: Hull Cell experimentsAluminum Plating Experiment 1

[0075] An example of the aluminum plating process used 0.3 M Al(Tf₂N)₃ in water with an additional electrolyte of 1 M ammonium acetate. An additive of 0.5 wt% PVA was added. A hull cell plating was conducted using 100 mL of the solution at 0.5 A for 30 mins giving a powdery deposit at the high current density end, no plating at the low current density end and a smooth, reflective, metallic coating between 40 A/dm² and 150 A/dm². The pH of the plating solution was buffered between 4.8 and 5.0, and a temperature of 40°C. The solution is found to contain some dark colored precipitate and a large amount of foaming, post electrolysis. A dark, metallic deposit of smooth reflective aluminum is shown by scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectroscopy analysis. See, e.g., FIG. 5.

Aluminum Plating Experiment 2

[0076] An additional example of the aluminum plating process used 0.3 M $\text{Al}(\text{Tf}_2\text{N})_3$ in water with an additional electrolyte of 1 M ammonium citrate which was titrated from 1M citric acid with NH_4OH . An additive of 0.5 w% PVA was added. A hull cell plating was conducted using 100 mL of the solution at 0.5 A for 30 mins giving a thicker and darker deposit at the high current density end (above 40 A/dm^2), no plating at the low current density (below 40 A/dm^2). The coating was thickest at the high current density end and appeared shiny and metallic. The pH of the plating solution was buffered between 2.8 and 3.2, and a temperature of 40°C. The solution is found to contain less dark colored precipitate but no foaming was seen in this case, post electrolysis. A thin, dark, metallic deposit of smooth reflective aluminum is shown by SEM and EDX analysis, with a clear deposition gradient from high to low current density.

Example 4: Small scale electroplating of high purity aluminum from $\text{Al}(\text{OMs})/\text{NH}_4$ Citrate on a curved geometry

[0077] Using a 10 mL test aliquot of 0.5 M $\text{Al}(\text{OMs})$ and 1 M ammonium citrate with aluminum to ligand ratio of 1:1, a 20 AWG copper wire was successfully plated to a thickness in excess of 10 μm . The procedure used a two electrode system with a copper wire (20 AWG, 6mm length) as the cathode substrate and an aluminum counter / reference electrode. Chronopotentiometry was carried out at -20 mA (-120 $\text{mA}\cdot\text{cm}^{-2}$) for 3 hours (FIG. 5). The temperature of the bath was controlled and maintained at 54 °C throughout.

Example 5

[0078] A range of aluminum salts with various ligand structures have been developed (see Table 2). The ligands are generally considered as mono-dentate, with the exception of Tf_2N which is more likely a bidentate ligand. Each ligand is considered as electron withdrawing in nature to varying degrees. While not being bound by any specific theory, it is believed that this electron withdrawing character is likely to shift the reduction potential of aluminum (or any other metal described herein) with the most strongly electron withdrawing substituents leading to a shift towards less negative potentials. FIG. 2 shows the comparative electron withdrawing character of each substituent as estimated from the

pKa of the acid. Generally speaking, stronger acids are more able to stabilize the deprotonated form of the acid leading to lower pKas.

[0079] In order to test the effect of various electron withdrawing substituents on the standard reduction potential of aluminum complexes a series of cyclic voltammetry experiments were carried out. Each salt was synthesized *in situ* by combination of various acids with aluminum carbonate in water to make a 1 M solution of each salt. In order to limit ligand substitution and complexation, no other electrolyte was added into the solution. Each cyclic voltammogram was collected vs. Ag/AgCl (3 M NaCl) and used an aluminum counter electrode. The working electrode was chosen as glassy carbon to limit the hydrogen evolution reaction which would ordinarily obscure the aluminum reduction for some salts.

[0080] As a control case 1 M AlCl_3 was used to gauge the effectiveness of the electron withdrawing substituents. It was expected that for aluminum chloride it is likely that the electroactive species is of an aqueous aluminum hydroxide complex ($\text{Al}[\text{H}_2\text{O}]_5\text{OH}$), which forms rapidly upon AlCl_3 exposure to excess water. This aluminum complex was initially compared to $\text{Al}(\text{Tf}_2\text{N})_3$ (FIG. 2) and it was found that the electron withdrawing Tf_2N ligands had a significant effect on the cathodic reduction process. The onset potential was shifted from about -1.65 V to about -1.1 V. While not being bound by any particular theory, it is believed that this shift in reduction potential shows that the aluminum species may be in a different form from the AlCl_3 case and does not simply become a water hydroxide complex. This might suggest that the ligand structure might be substantially retained in water and remains stable in solution for months. This development in aqueous aluminum complexation and comparative ease of electroreduction allows for greater competition of aluminum reduction with hydronium reduction on metal substrates, thus opening an aqueous aluminum plating procedure. Further evidence that aluminum electroplating is possible in this system comes from the presence of a nucleation loop in a reverse scan. This suggests a nucleation event occurs on the cathodic wave, likely the surface adsorption of a reduced aluminum species.

[0081] Additional salts (see Table 2) have been tested in a similar procedure with some salts showing similar promise for aluminum reduction. Other ligands were tested in a 1:1, 1:3 and 1:6 ratio of aluminum to ligand to test the effect of a 6 coordinate complex vs. a

1 or 3 coordinate complex. In the case of a hexa-coordinate aluminum species, an additional effect was that excess acid caused the pH to be reduced significantly.

[0082] When p-TSA is used as the ligand in both a 1:4 and 1:6 ratio with Al^{3+} a systematic shift is seen towards more positive reduction potentials. As the solution becomes more acidic, it would be expected that hydronium reduction would become more prevalent at more positive potentials. In the case of 6 M unbound p-TSA (FIG. 3 scan (i)) a solvent reduction wave is visualized with a low onset and no mass transport limiting peak. When the same amount of p-TSA is used in a 1:6 molar ratio with aluminum a similar onset is seen (FIG. 3 scan (ii)) but now a peak emerges which, when compared with $\text{Al}(\text{Tf}_2\text{N})_3$ may be attributed to an Al^{3+} reduction event from a p-TSA rich complex. In a 1:4 ratio with aluminum (FIG. 3 scan (iii)), a more negative onset and peak is seen as well as larger resistance. This discrepancy may be explained in part by pH shift since it would be expected that the excess acid would lead to a dramatic reduction in solution pH. Indeed, the pH of the 1:6 solution is about 0.24 and may explain the early onset of hydronium reduction. When the pH of this solution was adjusted by addition of ammonium hydroxide to pH 1.35 the redox behavior is identical to that of the 1:4 solution (FIG. 3, scans (iii) and (iv)). This behavior shows that the redox process is the same in both cases and that the aluminum coordination is likely by 1-4 p-TSA, is stable in acidic media and has a lower reduction potential than $\text{Al}(\text{H}_2\text{O})\text{OH}^{2+}$.

[0083] Methanesulfonate (MS) is a comparable ligand to p-TSA, showing highly electron withdrawing character but is sterically much smaller, which may be expected to facilitate a hexa-coordinate aluminum species. It is found that both the 1:1 and 6:1 ligand to aluminum ratio cases have very similar onsets for aluminum reduction of ca. -1.1V. However the 3:1 case shows an onset of only -0.84 V. This suggests that a maximized effect for electron withdrawing ligands is found for this ratio with lower coordination (1:1) being very similar in onset to other tested ligands and 6:1 having an excess of acid and ligands. The 3:1 case also has a pH of only 2.47 suggesting that a lot of the expected free protons are lost upon reaction with the carbonate and the ligands are likely coordinated rather than the aluminum complex leading to a high hydronium ion concentration.

[0084] Triflate (TfO) showed very little evidence of ligation to aluminum with a 6:1 ratio of acid showing a highly acidic environment with a pH of 0. This suggests that the

majority of the acid remains free and is not involved in the anticipated carbonate displacement reaction and leads to almost no aluminum ligation. This hypothesis is corroborated by the relatively negative reduction potential compared to other ligands of -1.35 V.

[0085] The final ligand Trifluoroacetate (TFA) was different from the others by way of a coordinating acetate anion rather than a sulfonate. For the case of a 1:3 complex for aluminum to TFA, a similar character was seen to that of both p-TSA and TfO with an onset potential of ca -1.10 V and a resistive peak being found, suggesting very few charge carriers being available. With a 1:6 ratio of aluminum to TFA a much lower onset potential was found although it is highly likely that the majority of this process was proton reduction with no clear aluminum onset being detectable. When the pH was adjusted for the 1:6 solution to make it most similar to that of the 1:3 a much higher onset potential was found. This suggests a different reductive aluminum species as compared to the 1:3 case, although the reduction was also not similar in character to that of $\text{Al}(\text{H}_2\text{O})_5\text{OH}$ and thus it must be determined that TFA is able to at least partially coordinate to the aluminum center and affect its electronegativity.

86] In summary, $\text{Al}(\text{MS})_3$ shows the lowest recorded potential for Al^{3+} reduction below that for hydronium reduction with an onset of about -0.84 V and a peak at about -1.3 V. See, e.g., FIG. 4. Hydrogen generation is obvious at the higher limit of this voltage range but an appreciable current for aluminum reduction is established prior to the evolution of gas. Other ligands p-TSA and Tf_2N show a comparable lowered reduction potential although slightly more negative than MS. It is unclear what the coordination for the p-TSA ligand is to aluminum, and is likely to be able to coordinate at least three p-TSA ligands. This coordination is sufficient to substantially lower the reduction potential of Al^{3+} and is visible proceeding hydronium reduction at pHs as low as 1.35. TfO however, seems to be unstable in the presence of NH_4^+ and is likely not strongly coordinating, with a redox process most similar to that of the water hydrated aluminum species. TFA appears to be an intermediate case whereby a lower coordination number may be possible in conjunction with some hydration. A slightly improved reduction potential is recorded, although not sufficient to compete with either Tf_2N or p-TSA.

[0087] It will be apparent to those skilled in the art that the specific structures, features, details, configurations, etc., that are disclosed herein are simply examples that can be modified and/or combined in numerous embodiments. All such variations and combinations are contemplated by the inventor as being within the bounds of this disclosure. Thus, the scope of the disclosure should not be limited to the specific illustrative structures described herein, but rather extends at least to the structures described by the language of the claims, and the equivalents of those structures.

[0088] The present invention provides for the following exemplary embodiments, the numbering of which is not to be construed as designating levels of importance:

[0089] Embodiment 1 relates to a method for the electrodeposition of at least one metal onto a surface of a conductive substrate at a temperature from about 10°C to about 70°C, about 0.5 atm to about 5 atm, in an atmosphere comprising oxygen, the method comprising electrodepositing the at least one metal via electrochemical reduction of a metal complex dissolved in a substantially aqueous medium.

[0090] Embodiment 2 relates to the method of Embodiment 1, wherein the metal comprises at least one of reactive and non-reactive metals.

[0091] Embodiment 3 relates to the method of Embodiment 2, wherein the reactive metal comprises at least one of aluminum, titanium, manganese, gallium, vanadium, zinc, zirconium, and niobium.

[0092] Embodiment 4 relates to the method of Embodiment 2, wherein the non-reactive metal comprises at least one of tin, gold, copper, silver, rhodium, and platinum.

[0093] Embodiment 5 relates to the method of Embodiments 1-4, wherein the metal complex comprises a metal center and ligands, wherein at least one of the ligands is an electron withdrawing ligand

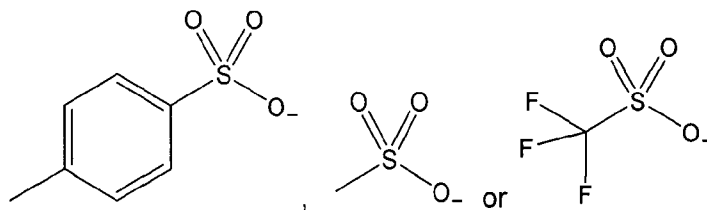
[0094] Embodiment 6 relates to the method of Embodiment 5, wherein the ligands are sufficiently electron withdrawing such that the reduction potential of the metal in the metal complex is decreased below the over-potential for the evolution of hydrogen gas due to water splitting.

[0095] Embodiment 7 relates to the method of Embodiments 5-6, wherein the ligands are at least one of sulfonate ligands and sulfonimide ligands.

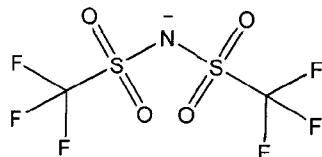
[0096] Embodiment 8 relates to the method of Embodiment 7, wherein the at least one sulfonate ligands is a ligand of the formula SO_3R^1 , wherein R^1 is halo; substituted or unsubstituted $\text{C}_6\text{-C}_{18}\text{-aryl}$; substituted or unsubstituted $\text{C}_1\text{-C}_6\text{-alkyl}$; substituted or unsubstituted $\text{C}_6\text{-C}_{18}\text{-aryl-C}_1\text{-C}_6\text{-alkyl}$.

[0097] Embodiment 9 relates to the method of Embodiment 7, wherein the at least one sulfonimide ligand is a ligand of the formula $\text{N}(\text{SO}_3\text{R}^1)$, wherein R^1 is halo; substituted or unsubstituted $\text{C}_6\text{-C}_{18}\text{-aryl}$; substituted or unsubstituted $\text{C}_1\text{-C}_6\text{-alkyl}$; substituted or unsubstituted $\text{C}_6\text{-C}_{18}\text{-aryl-C}_1\text{-C}_6\text{-alkyl}$.

[0098] Embodiment 10 relates to the method of Embodiment 7-9, wherein the at least one sulfonate ligand comprises a sulfonate ligand of the formulae:



[0099] Embodiment 11 relates to the method of Embodiment 7, wherein the at least one sulfonimide ligand comprises a sulfonimide ligand of the formula:



[00100] Embodiment 12 relates to the method of Embodiments 1-11, wherein the metal complex is at least one metal complex of the formula $\text{Al}(\text{SO}_3\text{R}^1)_n$, wherein R^1 is halo; substituted or unsubstituted $\text{C}_6\text{-C}_{18}\text{-aryl}$; substituted or unsubstituted $\text{C}_1\text{-C}_6\text{-alkyl}$; substituted or unsubstituted $\text{C}_6\text{-C}_{18}\text{-aryl-C}_1\text{-C}_6\text{-alkyl}$; n is an integer from 2 to 8; and $\text{Al}[\text{N}(\text{SO}_3\text{R}^1)_2]_n$, wherein R^1 is halo; substituted or unsubstituted $\text{C}_6\text{-C}_{18}\text{-}$; substituted or unsubstituted $\text{C}_1\text{-C}_6\text{-alkyl}$; substituted or unsubstituted $\text{C}_6\text{-C}_{18}\text{-aryl-C}_1\text{-C}_6\text{-alkyl}$; and n is an integer from 1 to 4.

[00101] Embodiment 13 relates to the method of Embodiments 1-12, wherein the substantially aqueous medium comprises an electrolyte.

[00102] Embodiment 14 relates to the method of Embodiment 13, wherein the electrolyte comprises at least one of a halide electrolyte; a perchlorate electrolyte; an amidosulfonate electrolyte; hexafluorosilicate electrolyte; a tetrafluoroborate electrolyte; methanesulfonate electrolyte; and a carboxylate electrolyte.

[00103] Embodiment 15 relates to the method of Embodiments 13-14, wherein the electrolyte comprises at least one of compounds of the formula $R^3CO_2^-$, wherein R^3 is substituted or unsubstituted C_6-C_{18} -aryl; or substituted or unsubstituted C_1-C_6 -alkyl;

[00104] Embodiment 16 relates to the method of Embodiments 13-15, wherein the electrolyte comprises at least one of polycarboxylates; and lactones.

[00105] Embodiment 17 relates to the method of Embodiments 1-16, wherein the pH of the substantially aqueous medium is buffered at a pH of about 1 and about 7.

[00106] Embodiment 18 relates to the method of Embodiments 1-17, wherein the substantially aqueous medium comprises a water-miscible organic solvent.

[00107] Embodiment 19 relates to the method of Embodiment 18, wherein the water-miscible organic solvent comprises at least one of an C_1-C_6 -alkanol, a C_2-C_{10} -polyol, a (poly)alkylene glycol ether, a C_2-C_{10} -carboxylic acid; a C_2-C_{10} -ketone; a C_2-C_{10} -aldehyde; a pyrrolidone; a C_2-C_{10} -nitrile; a phthalate; a C_2-C_{10} -dialkylamine; a C_2-C_{10} -dialkylformamide; a C_2-C_{10} -dialkyl sulfoxide; a C_4-C_{10} -heterocycloalkane; an aminoalcohol; and a C_4-C_{10} -heteroarylene.

[00108] Embodiment 20 relates to the method of Embodiment 19, wherein the C_1-C_6 -alkanol comprises ethanol.

[00109] Embodiment 21 relates to the method of Embodiments 1, wherein the electrodepositing comprises electrodepositing at least one layer of the at least one metal onto a surface of the substrate.

[00110] Embodiment 22 relates to the method of Embodiments 1-21, wherein the electrodepositing comprises electrodepositing at least two layers of the at least one metal onto a surface of the substrate.

[00111] Embodiment 23 relates to the method of Embodiment 22, wherein the first layer comprises different at least one metal relative to the second layer.

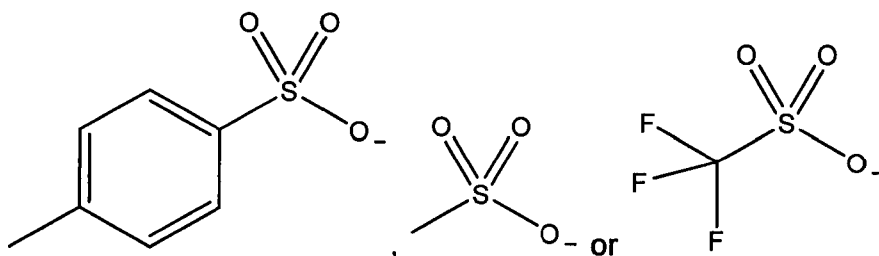
CLAIMS

1. A method for the electrodeposition of aluminum onto a surface of a conductive substrate at a temperature from 10°C to 70°C, 0.5 atm (50.66 kPa) to 5 atm (506.62 kPa), in an atmosphere comprising oxygen, the method comprising electrodepositing the aluminum via electrochemical reduction of an aluminum complex dissolved in an aqueous medium, the aluminum complex comprising an aluminum center and ligands;

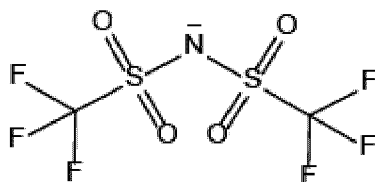
wherein:

the ligands are at least one of sulfonate ligands and sulfonimide ligands.

2. The method according to claim 1, wherein the at least one sulfonate ligand is a ligand of the formula SO_3R^1 , wherein R^1 is halo; substituted or unsubstituted $\text{C}_6\text{-C}_{18}$ -aryl; substituted or unsubstituted $\text{C}_1\text{-C}_6$ -alkyl; or substituted or unsubstituted $\text{C}_6\text{-C}_{18}$ -aryl- $\text{C}_1\text{-C}_6$ -alkyl.
3. The method according to claim 1, wherein the at least one sulfonimide ligand is a ligand of the formula $\text{N}(\text{SO}_3\text{R}^1)$, wherein R^1 is halo; substituted or unsubstituted $\text{C}_6\text{-C}_{18}$ -aryl; substituted or unsubstituted $\text{C}_1\text{-C}_6$ -alkyl; or substituted or unsubstituted $\text{C}_6\text{-C}_{18}$ -aryl- $\text{C}_1\text{-C}_6$ -alkyl.
4. The method according to claim 1, wherein the at least one sulfonate ligand comprises a sulfonate ligand of the formulae:



5. The method according to claim 1, wherein the at least one sulfonimide ligand comprises a sulfonimide ligand of the formula:



6. The method according to claim 1, wherein the aluminum complex is at least one aluminum complex of the formula $\text{Al}(\text{SO}_3\text{R}^1)_n$, wherein R^1 is halo; substituted or unsubstituted $\text{C}_6\text{-C}_{18}$ -aryl; substituted or unsubstituted $\text{C}_1\text{-C}_6$ -alkyl; or substituted or unsubstituted $\text{C}_6\text{-C}_{18}$ -aryl- $\text{C}_1\text{-C}_6$ -alkyl; n is an integer from 2 to 8; and $\text{Al}[\text{N}(\text{SO}_3\text{R}^1)_2]_n$, wherein R^1 is halo; substituted or unsubstituted $\text{C}_6\text{-C}_{18}$ -aryl; substituted or unsubstituted $\text{C}_1\text{-C}_6$ -alkyl; or substituted or unsubstituted $\text{C}_6\text{-C}_{18}$ -aryl- $\text{C}_1\text{-C}_6$ -alkyl; and n is an integer from 1 to 4.
7. The method according to claim 1, wherein the aqueous medium comprises an electrolyte.
8. The method according to claim 7, wherein the electrolyte comprises at least one of a halide electrolyte; a perchlorate electrolyte; an amidosulfonate electrolyte; hexafluorosilicate electrolyte; a tetrafluoroborate electrolyte; methanesulfonate electrolyte; and a carboxylate electrolyte.
9. The method according of claim 8, wherein the electrolyte comprises at least one of compounds of the formula R^3CO_2^- , wherein R^3 is substituted or unsubstituted $\text{C}_6\text{-C}_{18}$ -aryl; or substituted or unsubstituted $\text{C}_1\text{-C}_6$ -alkyl.
10. The method according to claim 8, wherein the electrolyte comprises at least one of polycarboxylates and lactones.
11. The method according to claim 1, wherein the pH of the aqueous medium is buffered at a pH from 1 to 7.
12. The method according to claim 1, wherein the aqueous medium comprises a water-miscible organic solvent.
13. The method according to claim 12, wherein the water-miscible organic solvent comprises at least one of an $\text{C}_1\text{-C}_6$ -alkanol, a $\text{C}_2\text{-C}_{10}$ -polyol, a (poly)alkylene glycol ether, a $\text{C}_2\text{-C}_{10}$ -carboxylic acid; a $\text{C}_2\text{-C}_{10}$ -ketone; a $\text{C}_2\text{-}$

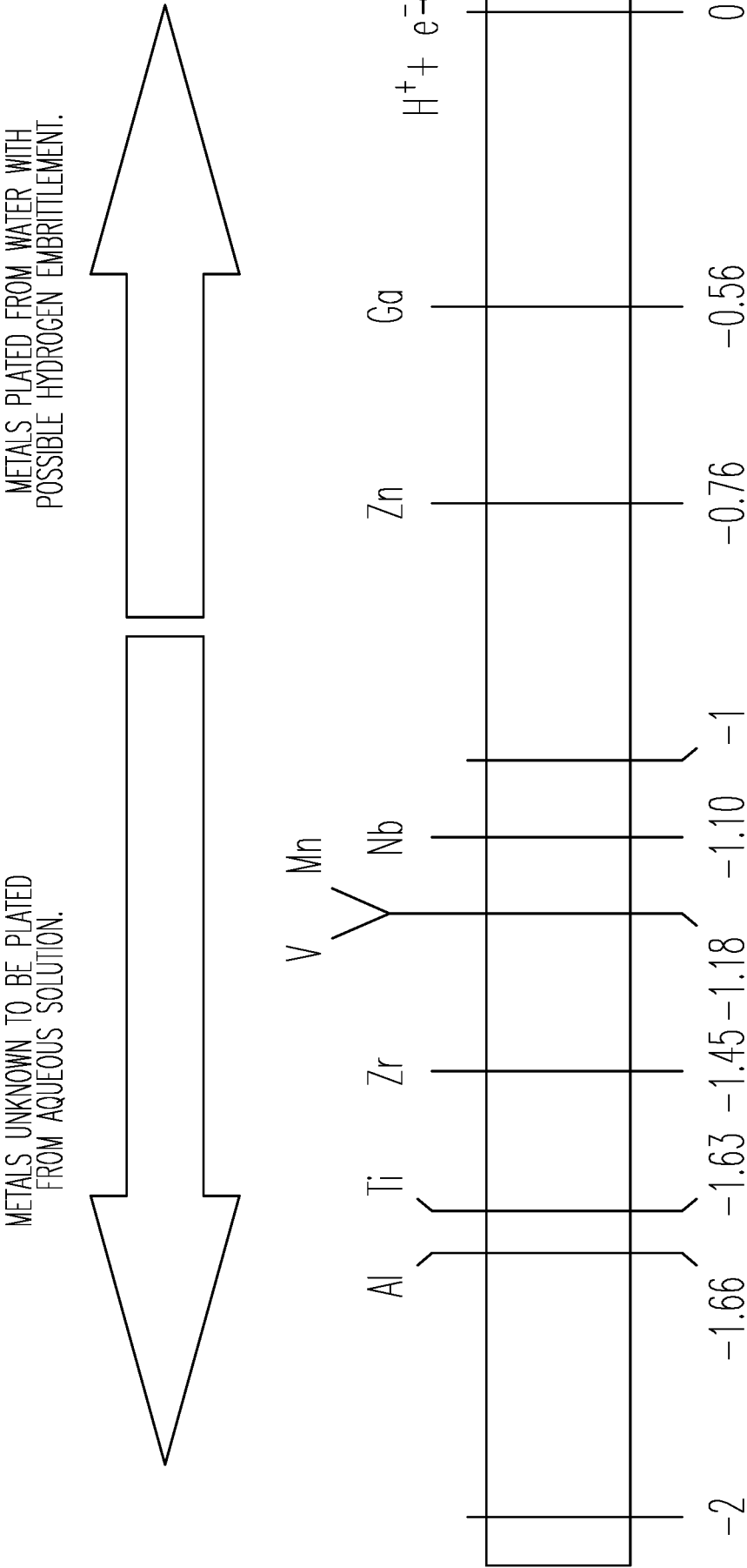
C₁₀-aldehyde; a pyrrolidone; a C₂-C₁₀-nitrile; a phthalate; a C₂-C₁₀-dialkylamine; a C₂-C₁₀-dialkylformamide; a C₂-C₁₀-dialkyl sulfoxide; a C₄-C₁₀-heterocycloalkane; an aminoalcohol; and a C₄-C₁₀-heteroarylene.

14. The method according to claim 13, wherein the C₁-C₆-alkanol comprises ethanol.
15. The method according to claim 1, wherein the electrodepositing comprises electrodepositing at least one layer of the aluminum onto the surface of the conductive substrate.
16. The method according to claim 1, wherein the electrodepositing comprises electrodepositing at least two layers of the aluminum onto the surface the conductive substrate.
17. A method for the electrodeposition of aluminum onto a surface of a conductive substrate at a temperature from 10°C to 70°C, 0.5 atm (50.66 kPa) to 5 atm (506.62 kPa), in an atmosphere comprising oxygen, the method comprising electrodepositing the aluminum via electrochemical reduction of an aluminum complex dissolved in an aqueous medium;
wherein:
the aluminum complex comprises an aluminum center and ligands, wherein at least one of the ligands is an electron withdrawing ligand, and is electron withdrawing such that the reduction potential of the aluminum in the aluminum complex is decreased below the over-potential for the evolution of hydrogen gas due to water splitting.
18. A method for the electrodeposition of aluminum onto a surface of a conductive substrate at a temperature from 10°C to 70°C, 0.5 atm (50.66 kPa) to 5 atm (506.62 kPa), in an atmosphere comprising oxygen, the method comprising electrodepositing the aluminum via electrochemical reduction of an aluminium complex dissolved in an aqueous medium that is at least about 50% aqueous, the aluminum complex comprising an aluminum center and ligands;

wherein:

the ligands are at least one of sulfonate ligands and sulfonimide ligands.

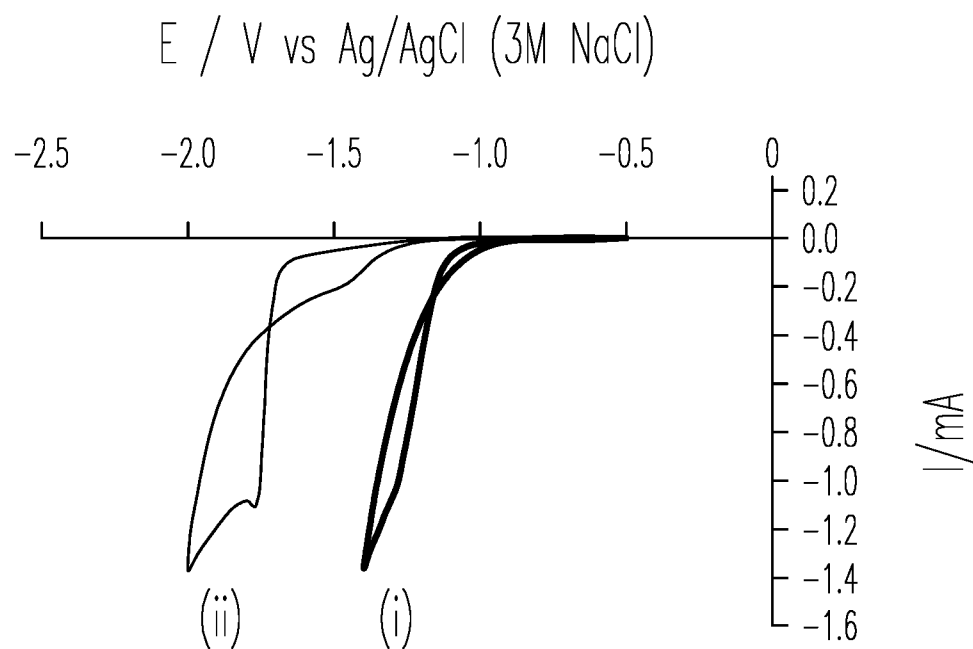
19. The method according to claim 18, wherein the medium is at least about 60% aqueous.
20. The method according to claim 19, wherein the medium is at least about 70% aqueous.
21. The method according to claim 20, wherein the medium is at least about 80% aqueous.
22. The method according to claim 21, wherein the medium is at least about 90% aqueous.
23. The method according to claim 22, wherein the medium is at least about 99% aqueous.
24. The method of claim 1, wherein the aqueous medium is water.



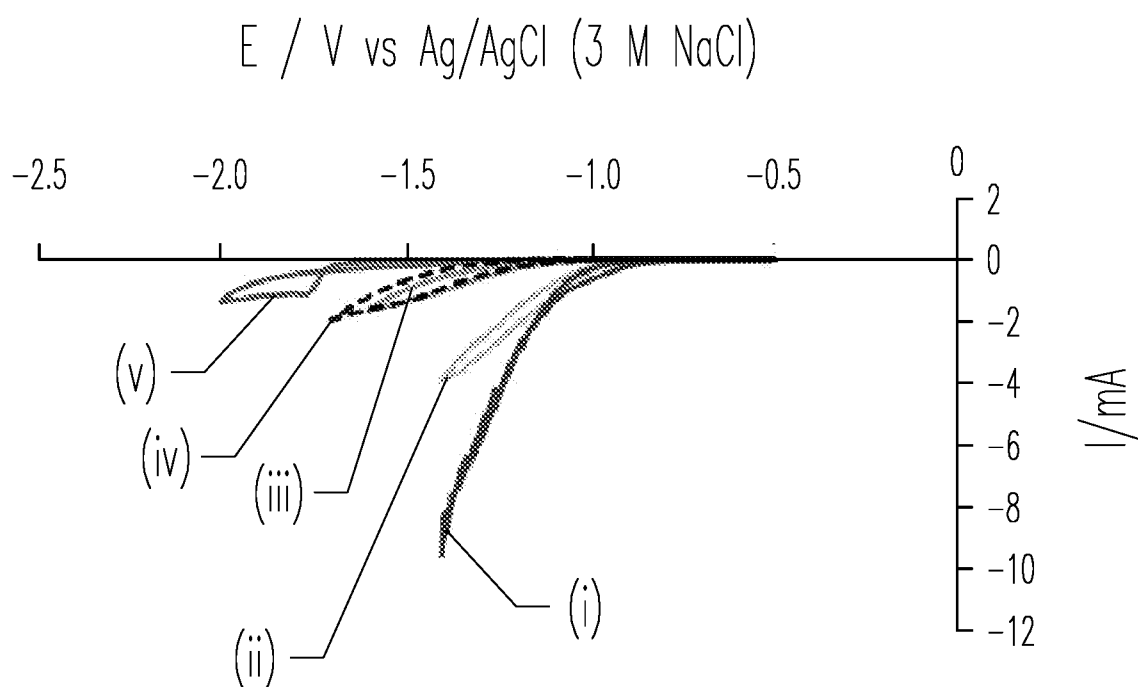
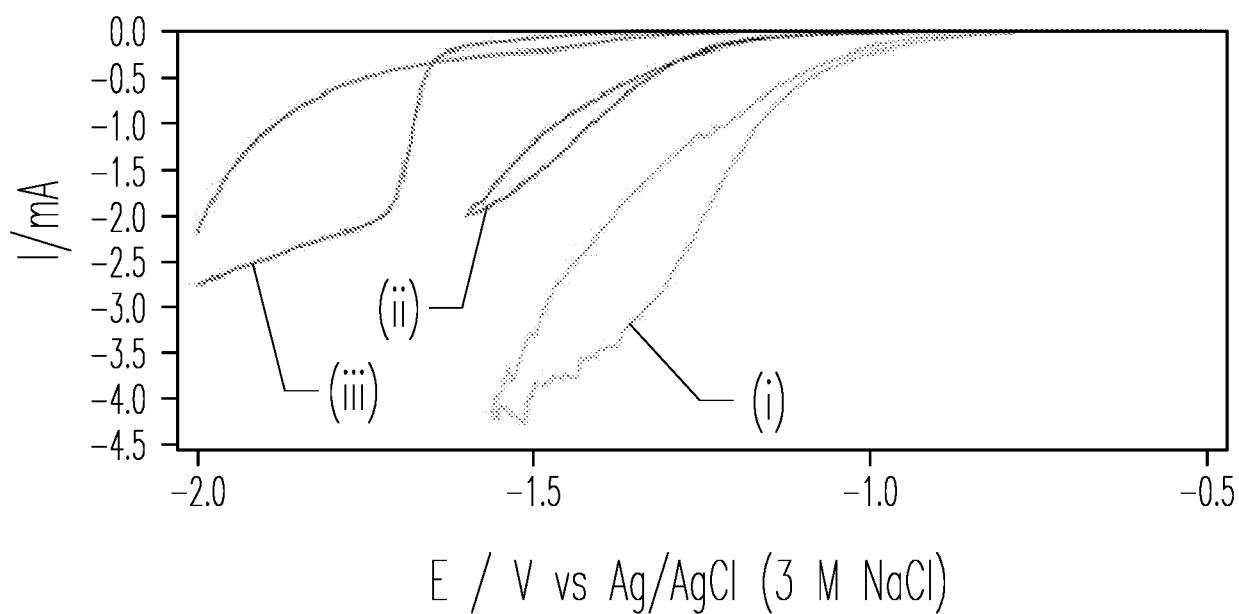
STANDARD ELECTRODE POTENTIAL / V
 $(M^{n+} + ne^- \rightarrow M(s))$

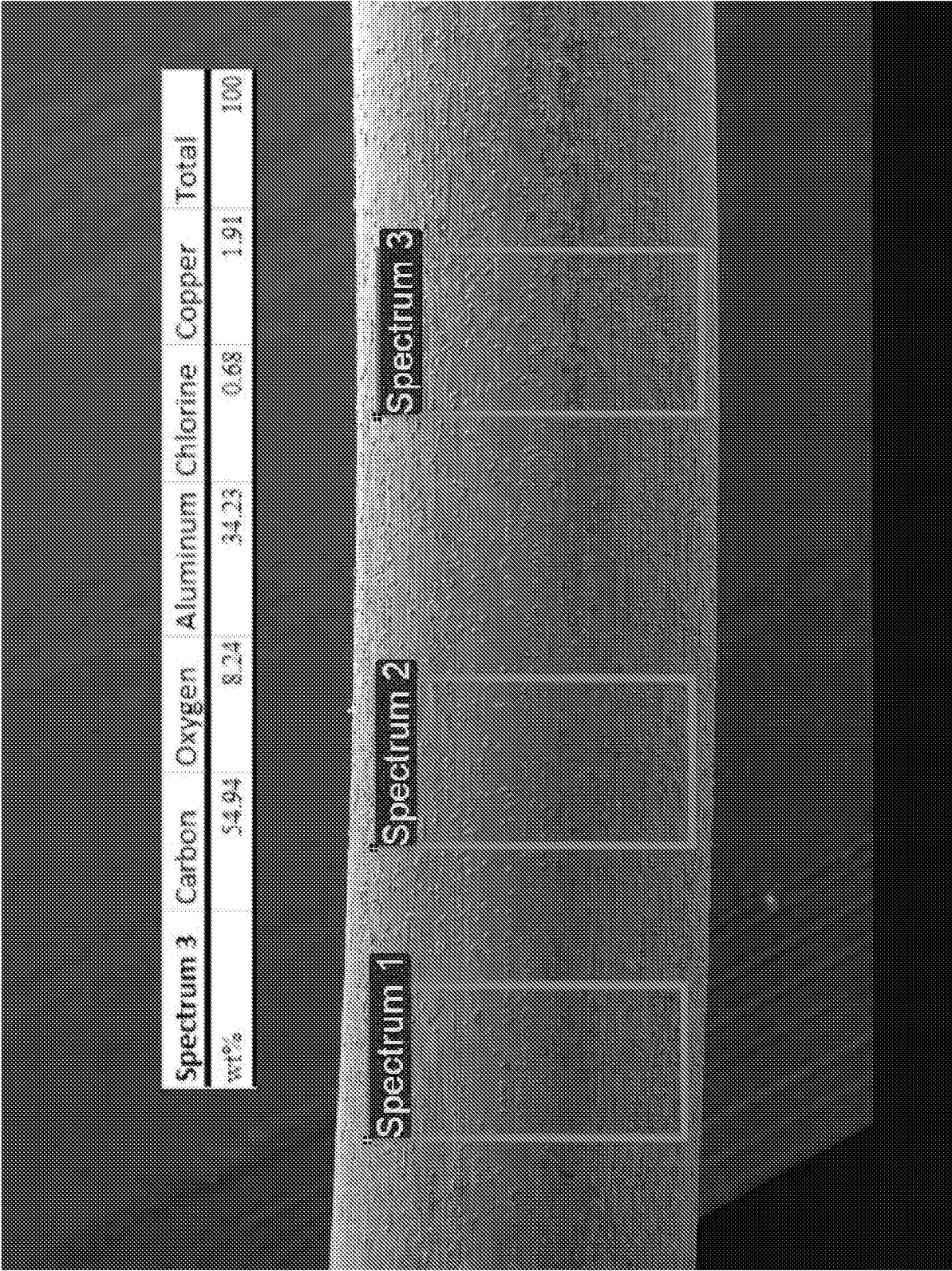
Fig. 1

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*Fig. 2*

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*Fig. 3**Fig. 4*



ELECTRON IMAGE 1

Fig. 5

$E / \text{V vs Ag/AgCl (3M NaCl)}$

