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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
5 February 2009 (05.02.2009)

PCT

(10) International Publication Number
WO 2009/016189 A1

(51) International Patent Classification:
C25D 3/66 (2006.01) *C25F 3/16* (2006.01)
C25D 3/02 (2006.01)

(21) International Application Number:
PCT/EP2008/059962

(22) International Filing Date: 30 July 2008 (30.07.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
07113717.8 2 August 2007 (02.08.2007) EP
60/954,434 7 August 2007 (07.08.2007) US

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

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

Published:
— *with international search report*

(54) Title: METHOD TO ELECTRODEPOSIT METALS USING IONIC LIQUIDS IN THE PRESENCE OF AN ADDITIVE

(57) Abstract: The present invention pertains to the use of an additive selected from the group consisting of amorphous silica, graphite powder, and a mixture thereof in a process to electroplate or electropolish a metal on a substrate using an ionic liquid as the electrolyte to increase metal layer thickness. It furthermore pertains to a method to electroplate or electropolish a metal on a metal substrate wherein an ionic liquid is employed as electrolyte, wherein a metal salt added to said ionic liquid or a metal anode is employed as metal source, and wherein said ionic liquid comprises said additive.

WO 2009/016189 A1

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METHOD TO ELECTRODEPOSIT METALS USING IONIC LIQUIDS IN THE PRESENCE OF AN ADDITIVE

The present invention relates to a method to electrodeposit a metal on a substrate using an ionic liquid as the electrolyte in the presence of an additive, and to the use of said additive to increase the layer thickness of the deposited metal layer.

An ionic liquid is a salt in which the ions are poorly coordinated, which results in these solvents being liquid at temperatures below 100°C. Many are liquid even at room temperature. At least one ion in an ionic liquid has a delocalized charge and one component is organic, which prevents the formation of a stable crystal lattice. Ionic liquids generally have very low vapour pressure and thus, in contrast to many conventional solvents, produce virtually no hazardous vapours. It is known that, in general, ionic liquids may be used in many applications, e.g. as reaction solvents, extraction solvents, electrolytes in batteries and electrodeposition, catalysts, heat exchange fluids, as additives in coatings.

Well-known systems include those formed from alkylpyridinium halides or dialkylimidazolium halides with an aluminium halide, and those based on choline chloride and a (hydrated) metal salt such as chromium(III) chloride. These systems have been utilized as electrolytes in electroplating, as described for example in EP 0 404 188 and EP 1 322 591.

Further, WO 2002/026381 discloses ionic liquids (eutectic mixtures) of choline chloride and a (hydrated) metal salt such as chromium(III) chloride and the use thereof in electrodeposition and electropolishing. The mixtures consist of choline chloride and the (hydrated) metal salt in a ratio of ammonium to metal ion of between 1:1 and 1:2.5 and are specifically said to be suitable for depositing chromium, cobalt, zinc or silver on a metal substrate.

Moreover, PCT/EP/2007/051329 describes a method to electroplate or electropolish a metal on a substrate wherein an ionic liquid selected from the group of

$N^+R_1R_2R_3R_4\ X^-$ or

$N^+R_5R_6R_7R_8\ Y^-$

is employed as electrolyte, and a metal salt added to the ionic liquid is employed as the metal source or a metal anode is used as the metal source, wherein any one of R_1 to R_8 independently represents a hydrogen, alkyl, cycloalkyl, aryl, or aralkyl group that may be substituted with a group selected from OH, Cl, Br, F, I, phenyl, NH_2, CN, NO_2, $COOR_9$, CHO, COR_9, or OR_9, at least one of R_5 to R_8 is a fatty alkyl chain, and one or more of R_5 to R_8 can be a (poly)oxyalkylene group wherein the alkylene is a C_1 to C_4 alkylene and the total number of oxyalkylene units can be from 1 to 50 oxyalkylene units, and at least one of R_1 to R_8 is a C_1 to C_4 alkyl chain, R_9 is an alkyl or cycloalkyl group, X^- is an anion having an N-acyl sulphonylimide anion ($-CO-N^--SO_2-$) functionality, Y^- is an anion compatible with the $N^+R_5R_6R_7R_8$ ammonium cation, such as a halogenide anion, a carboxylate anion, a sulphate (both organic and inorganic sulphate), sulphonate, carbonate, nitrate, nitrite, thiocyanate, hydroxide, or sulphonylimide anion.

The use of ionic liquids as electrolytes in electrodeposition processes has several advantages. Conventional chromic acid plating processes, for example, are extremely hazardous because they mainly rely on hexavalent chromium, which is highly toxic and carcinogenic. Ionic liquids, on the other hand, may eliminate the necessity to use hexavalent chromium and allow the use of trivalent chromium, which is considered to be far less dangerous. Also, conventional chromium plating baths require the use of strong acids, which poses significant disposal problems, while the use of ionic liquids generally enables such disposal difficulties to be minimized or even eliminated. Moreover, ionic liquids are non-volatile, so they do not cause atmospheric pollution.

However, a drawback to the prior art electrodeposition processes wherein an ionic liquid is used as the electrolyte is that depositing metal layers of some metals thicker than 150-200 nm is difficult or even impossible.

For some applications, such as decorative plating, having thin metal layers is acceptable. However, for applications where the metal layer needs to provide protection against wear or abrasion, or to improve hardness (functional plating), metal layers much thicker than 200 nm are required. More particularly, layers of several micrometers or even several tens of micrometers are desirable.

Hence, there is a need for improved ionic liquid-based electrodeposition systems with which metal layers of increased thickness are deposited.

Surprisingly, it has been found that by adding a particular additive to the ionic liquid-based plating baths, thicker metal layers are deposited. In more detail, the present invention relates to the use of amorphous silica, graphite powder, or a mixture thereof as additive in a process to electroplate or electropolish a metal on a substrate wherein an ionic liquid is employed as the electrolyte to increase metal layer thickness.

Additives have been added to the ionic liquid comprising electrolyte for several reasons. US 7,196,221, for example, discloses the use of brightening agents to improve the appearance of the coatings obtained in ionic liquid solvents/-electrolytes during metal plating and electropolishing processes, and in particular in chromium plating processes. The brightening agents include thiourea, saccharin, vanillin, allyl urea, nicotinic acid, citric acid, gelatin, 2-mercaptobenzothiazole, tetraethylammonium fluoride dihydrate or tetramethyl-ammonium hydroxide pentahydrate. However, these additives have an adverse effect on the homogeneity of the deposited layer, or no effect at all.
WO 2006/074523 relates to a process for the recovery of platinum group metal, which comprises electrodeposition of the platinum group metal from an ionic

liquid wherein redox reagents, complexing agents, conductivity enhancers may be present.

US 6,552,843, which is concerned with devices, such as adjustable mirrors, smart windows, optical attenuators, and displays, for controlling the reflectance and/or transmission of electromagnetic radiation, discloses a reversible electrodeposition optical modulation device employing an ionic liquid electrolyte. The ionic liquid electrolyte is comprised of a mixture of an ionic organic compound and the salt of an electrodepositable metal. The ionic organic compound comprises a heterocyclic cation such as N-alkylpyrrolidinium, pyrrolidinium, 1-alkyl-3-methylimidazolium, N-alkylpyridinium, 2-alkyl-1-pyrrolinium, 1-alkylimidazolium. The electrodepositable metal is silver, copper, tin, zinc, palladium, bismuth, cadmium, mercury, indium, lead, antimony, thallium, and alloys thereof. It is mentioned that said ionic liquid electrolyte may be rendered more viscous, semi-solid or solid by addition of organic or inorganic gelling agents. Inorganic or organic materials, including suspended carbon and dissolved dyes, may be added to the electrolyte to impart a desired colour or to reduce background reflection.

None of these documents teaches how to obtain thicker metal layers in electrodeposition processes with ionic liquid comprising electrolytes.

The term electrodeposition in this application should be understood to include both electroplating and electropolishing. By electroplating is meant the process of using electrical current to coat an electrically conductive object with a layer of metal. The preferred result is a thin, smooth, even coat of metal on the object. The primary application of electroplating is to deposit a layer of a metal having some desired property (e.g., abrasion and wear resistance, corrosion protection, lubricity, improvement of aesthetic qualities, etc.) onto a surface lacking that property. Another application uses electroplating to build up thickness on undersized parts. By electropolishing is meant smoothing and enhancing the appearance of an originally rough or uneven metal surface by coating it with a relatively thin metal layer.

The additive used according to the present invention to increase the thickness of the deposited metal layer is amorphous silica, graphite powder, or a mixture thereof.

The term amorphous silica is meant to include colloidal silica particles in any form, where the colloidal silica particles, which are also referred to as silica sols, may be derived from e.g. precipitated silica, silica gels, pyrogenic silica (fumed silica), micro silica (silica fume) or mixtures thereof. Colloidal silica according to the present invention may be modified and can contain other elements such as amines, aluminium and/or boron, which can be present in the particles and/or the continuous phase.

The colloidal silica particles can be dispersed in a substantially aqueous solvent, suitably in the presence of stabilizing cations such as K^+, Na^+, Li^+, NH_4^+, organic cations, primary, secondary, tertiary, and quaternary amines, and mixtures thereof, so as to form an aqueous silica sol. However, also dispersions comprising organic solvents, e.g. lower alcohols, acetone or mixtures thereof, also denoted as organo-silica sols, may be used. Preferably, the silica content in the sol is from about 5 to about 80% by weight.

Aqueous silica sols suitable for use according to the present invention are e.g. commercially available from Akzo Nobel. Suitable organo-silica sols are e.g. commercially available from Nissan Chemical Industries.

By graphite powder is meant finely divided carbon powder or carbon black, e.g. commercially available from Degussa.

The additive is preferably used in a quantity of at least 0.01 wt%, more preferably of at least 0.05 wt%, and most preferably of at least 0.1 wt%, based on the total weight of the electrolyte. Preferably, no more than 5 wt%, more preferably no more than 3 wt%, and most preferably no more than 1 wt% of additive is used, based on the total weight of the electrolyte. It is noted that the term electrolyte stands for the total electrolyte mixture, i.e. including dissolved metal salts and additives.

With the present invention, *i.e.* with the addition of the described additive(s), the layer thickness can be increased at least 10 times, more preferably at least 20 times, and most preferably at least 40 times, when compared to electrodeposition without said additive(s).

The ionic liquid employed as electrolyte is preferably selected from the group consisting of $N^+R_1R_2R_3R_4\,X^-$, $N^+R_5R_6R_7R_8\,Y^-$, and mixtures thereof, wherein any one of R_1 to R_8 independently represents a hydrogen, alkyl, cycloalkyl, aryl, or aralkyl group that may be substituted with a group selected from OH, Cl, Br, F, I, phenyl, NH_2, CN, NO_2, $COOR_9$, CHO, COR_9, or OR_9, wherein at least one of R_1 to R_4 is an, optionally branched, fatty alkyl chain, wherein R_2 can be a (C_2-C_6 alkyl)-$N^+R_{16}R_{17}R_{18}$ group with R_{16}, R_{17}, R_{18} being similar to R_1, R_3, R_4, respectively, or a C_1 to C_4 alkyl chain, and wherein one or more of R_1 to R_8 can be a (poly)oxyalkylene group wherein the alkylene is a C_1 to C_4 alkylene and the total number of oxyalkylene units can be from 1 to 50 oxyalkylene units, and wherein at least one of R_1 to R_8 is a C_1 to C_4 alkyl chain, wherein R_9 is an alkyl or cycloalkyl group, wherein X^- is an anion compatible with the $N^+R_1R_2R_3R_4$ ammonium cation, such as a halogenide anion, a carboxylate anion, a sulphate (both organic and inorganic sulphate), sulphonate, carbonate, nitrate, nitrite, thiocyanate, hydroxide, saccharinate anion, or sulphonylimide anion, and wherein Y^- is an anion having a sulfonylimide anion or an N-acyl sulphonylimide anion ($-CO-N^--SO_2-$) functionality.

In one embodiment, X^- is selected from the group of F^-, Cl^-, Br^-, I^-; the group of $R_{10}COO^-$ anions wherein R_{10} may be hydrogen, a C_1-C_{22} alkyl, alkenyl or aromatic group; the group of $R_{11}SO_4^-$ anions wherein R_{11} may be absent, in which case the cation is divalent, hydrogen, a C_1-C_{22} alkyl, alkenyl or aromatic group; the group of $R_{12}SO_3^-$ anions wherein R_{12} may be absent, in which case the cation is divalent, hydrogen, a C_1-C_{22} alkyl, alkenyl or aromatic group; the group of $R_{13}CO_3^-$ anions wherein R_{13} may be absent, in which case the cation is divalent, hydrogen, a C_1-C_{22} alkyl, alkenyl or aromatic group; and the group of R_{14}-N^--SO_2-R_{15} anions wherein R_{14} and/or R_{15} independently may be hydrogen, a C_1-C_{22} alkyl, alkenyl or aromatic group, and R_{14} may be linked to the nitrogen atom with a carbonyl group.

A fatty alkyl chain is meant to include saturated and/or unsaturated chains and contains 8 to 22 carbon atoms; preferably, it contains 10 to 22 carbon atoms, most preferably 12 to 20 carbon atoms.

In another embodiment, an ionic liquid of the formula $N^+R_1R_2R_3R_4\ X^-$ is used with R_1, R_3, and R_4 being as mentioned above and with R_2 being a (C_2-C_6 alkyl)-$N^+R_{16}R_{17}R_{18}$ group. Preferably, R_{16}, R_{17}, and R_{18} are identical to R_1, R_2 and R_4, respectively, with at least one of them being an, optionally branched, fatty alkyl chain, resulting in a gemini-type structure (i.e. a symmetrical diquaternary ammonium compound).

In another embodiment, Y^- is based on a compound known as a sweetener. In another embodiment, $N^+R_5R_6R_7R_8$ is an amine wherein the groups R_5 to R_8 are hydrogen or an alkyl or cycloalkyl, optionally substituted with OH or Cl; more preferably, at least three thereof are an alkyl, more preferably a C_1 to C_4 alkyl.

In a preferred embodiment, the ionic liquid is selected from any one of choline saccharinate, choline acesulphamate, hexadecyltrimethyl ammonium chloride, octadecyltrimethyl ammonium chloride, cocotrimethyl ammonium chloride, tallowtrimethyl ammonium chloride, hydrogenated tallowtrimethyl ammonium chloride, hydrogenated palmtrimethyl ammonium chloride, oleyltrimethyl ammonium chloride, soyatrimethyl ammonium chloride, cocobenzyldimethyl ammonium chloride, C12-16-alkylbenzyldimethyl ammonium chloride, hydrogenated tallowbenzyldimethyl ammonium chloride, dioctyldimethyl ammonium chloride, didecyldimethyl ammonium chloride, dicocodimethyl ammonium nitrite, dicocodimethyl ammonium chloride, di(hydrogenated tallow)dimethyl ammonium chloride, di(hydrogenated tallow)benzylmethyl ammonium chloride, ditallowdimethyl ammonium chloride, dioctadecyldimethyl ammonium chloride, hydrogenated tallow(2-ethylhexyl)dimethyl ammonium chloride, hydrogenated tallow(2-ethylhexyl)dimethyl ammonium methylsulphate, trihexadecylmethyl ammonium chloride, octadecylmethylbis(2-hydroxyethyl) ammonium chloride, cocobis(2-hydroxyethyl)methyl ammonium nitrate, cocobis(2-hydroxyethyl)methyl ammonium chloride, cocobis(2-hydroxyethyl)benzyl ammonium chloride, oleylbis(2-hydroxyethyl)methyl ammonium chloride, coco[polyoxyethylene(15)]methyl ammonium chloride, coco[polyoxyethylene(15)]methyl ammonium methylsulphate, coco[polyoxyethylene(17)]methyl ammonium chloride, octadecyl-[polyoxyethylene(15)]methyl ammonium chloride, hydrogenated tallow[polyoxyethylene(15)]methyl ammonium chloride, tris(2-hydroxyethyl)tallow ammonium acetate, tallow-1,3-propane pentamethyl diammonium dichloride.

Many of the above-indicated ionic liquids suitable for use according to the present invention can be prepared by a simple reaction of salts, for example by a metathesis reaction of choline chloride and sodium saccharinate (acesulphamate) to form a choline saccharinate (acesulphamate) ionic liquid, or by quaternization of the corresponding amines.

The molar ratio of the ammonium cation of the ionic liquid to the metal cation of the metal salt, which comes from the dissolved salt or from the metal anode, is preferably between 1,000:1 and 3:1. More preferred is a molar ratio of the ammonium cation of the ionic liquid to the metal cation of the metal salt of between 500:1 and 5:1, most preferred is a molar ratio between 100:1 and 7:1, this providing a good-quality metal layer, excellent dissolution of the metal in the ionic liquid, and a good balance between the cost of the process and the appearance of the plated substrate product.

Preferably, one of the metals chromium, aluminium, titanium, zinc or copper, or an alloy thereof is deposited. More preferably, chromium or aluminium is deposited, most preferably chromium. This metal deposition can be done from a metal salt dissolved in the electrolyte, for example a metal halide, preferably, but not limited to, a metal chloride. It can also be performed using a pure metal which is applied as anode (*i.e.* a chromium, aluminium, titanium, zinc, or copper anode). In the embodiment where a metal anode is used, the anode may be in the form of metal pieces, chunks, chips or any other suitable form known to the skilled person.

The substrate which can be electroplated or electropolished according to the present invention can be any conductive object. Preferably, it is an object which is solid metal, such as a carbon steel object, or it comprises conductive elements such as a composite material object.

The present invention furthermore relates to a method to electroplate or electropolish a metal on a metal substrate wherein an ionic liquid ionic liquid is selected from the group consisting of $N^+R_1R_2R_3R_4\ X^-$, $N^+R_5R_6R_7R_8\ Y^-$, and mixtures thereof, wherein any one of R_1 to R_8 independently represents a hydrogen, alkyl, cycloalkyl, aryl, or aralkyl group that may be substituted with a group selected from OH, Cl, Br, F, I, phenyl, NH_2, CN, NO_2, $COOR_9$, CHO, COR_9, or OR_9, wherein at least one of R_1 to R_4 is an, optionally branched, fatty alkyl chain, wherein R_2 can be a (C_2-C_6 alkyl)-$N^+R_{16}R_{17}R_{18}$ group with R_{16}, R_{17}, R_{18} being similar to R_1, R_3, R_4, respectively, or a C_1 to C_4 alkyl chain, and wherein one or more of R_1 to R_8 can be a (poly)oxyalkylene group wherein the alkylene is a C_1 to C_4 alkylene and the total number of oxyalkylene units can be from 1 to 50 oxyalkylene units, and wherein at least one of R_1 to R_8 is a C_1 to C_4 alkyl chain, wherein R_9 is an alkyl or cycloalkyl group, wherein X^- is an anion compatible with the $N^+R_1R_2R_3R_4$ ammonium cation, such as a halogenide anion, a carboxylate anion, a sulphate (both organic and inorganic sulphate), sulphonate, carbonate, nitrate, nitrite, thiocyanate, hydroxide, saccharinate anion, or sulphonylimide anion, and wherein Y^- is an anion having a sulfonylimide anion or an N-acyl sulphonylimide anion ($-CO-N^--SO_2-$) functionality,

wherein a metal salt added to said ionic liquid or a metal anode is employed as metal source, and

wherein said ionic liquid comprises at least 0.01 wt%, based on the total weight of electrolyte, of an additive selected from the group consisting of amorphous silica, graphite powder, and of a mixture thereof.

The additive is preferably used in the quantities as described above.

The electrodeposition is preferably performed at temperatures below 90°C and more preferably at room temperature, in open electrodeposition vessels, but electrodeposition is not limited to these conditions.

The process according to the present invention is further illustrated by the following examples.

EXAMPLES

Comparative Example 1 – Electroplating of chromium from $CrCl_3$ hexahydrate salt onto carbon steel in cocoalkylmethyl [polyoxy-ethylene(15)] ammonium chloride with no additives

Chromium (III) chloride hexahydrate salt was added to cocoalkylmethyl [polyoxyethylene(15)] ammonium chloride ionic liquid containing 0.2 wt% of water and the mixture was agitated at a temperature of about 50°C until the solid salt dissolved. In the prepared solution the concentration of chromium (III) chloride hexahydrate was 75 g/kg.

About 250 ml of that solution was poured into the Hull cell equipped with an electrical heating element which had a length of 65 mm on the anode side and

102 mm on the cathode side, a 48 mm shortest anode-cathode distance, a 127 mm longest anode-cathode distance, and a depth of 65 mm. The cell was heated and the temperature was maintained at about 80°C. The liquid was agitated using a centrally positioned top-entering impeller.

Platinized titanium plate was applied as the anode and connected to the positive terminal of a DC power source, whereas carbon steel plate was used as the cathode (substrate) and connected to the negative terminal. Prior to introduction into the bath, the substrate plate was cleaned with a commercial scouring powder, washed in demineralized water, in acetone and after that in ethanol, and finally in a 4 M-HCl aqueous solution. When both plates were connected and introduced into the cell, the voltage difference was set to 30 V. The current flow was monitored on a meter connected in series.

After several hours of electroplating, the cathode was disconnected from the power source and taken out of the cell. The plate was washed in water and acetone and then dried. Chemical analysis by scanning electron microscopy combined with X-ray dispersion (SEM/EDX) of the substrate was performed. It confirmed deposition of chromium onto the carbon steel. The deposited layer thickness was measured using a thickness measurement device obtained from Fischer, Germany. The thickness was found to be lower than 0.5 μm.

Example 2 – Electroplating of chromium from $CrCl_3$ hexahydrate salt onto carbon steel in cocoalkylmethyl [polyoxyethylene(15)] ammonium chloride with addition of 0.2 wt% amorphous silica

To the prepared solution of chromium (III) chloride hexahydrate salt in cocoalkylmethyl [polyoxyethylene(15)] ammonium chloride ionic liquid as described in Example 1 was added an amorphous silica aqueous colloidal solution which contained 8 wt% of active compound. The concentration of the amorphous silica in the prepared solution, expressed as the quantity of the active compound, was 1.6 g/kg.

About 250 ml of that solution was poured into the Hull cell described in Example 1. The cell was heated to a temperature of about 80°C.

The same pretreatment of the carbon steel substrate (cathode) as in Example 1 was performed, and again platinized titanium plate was applied as the anode. The potential difference was set to 30 V. The liquid was agitated using a centrally positioned top-entering impeller. The current flow between the electrodes was monitored on a meter connected in series.

After several hours of submission to the current, the cathode was disconnected from the power source and taken out of the cell. The plate was washed in water and acetone and then dried. Chemical analysis by scanning electron microscopy combined with X-ray dispersion (SEM/EDX) of the substrate confirmed deposition of chromium onto the carbon steel plate. The deposited layer thickness, measured using a thickness measurement device (Fischer, Germany), was found to be as high as 8 μm in certain regions of the substrate, which was significantly thicker than when no additive was used. As is typical for the Hull cell experiments, the layer thickness varied with the position on the substrate – in this case from 1 μm to 8 μm. To confirm these measurements a cross-cut metallographic analysis was also done. The sample of the substrate was embedded in epoxy resin and the deposit was evaluated under the microscope. The layer thickness determined in this way was in agreement with the thickness measurement device results.

Example 3 – Electroplating of chromium from $CrCl_3$ hexahydrate salt onto carbon steel in cocoalkylmethyl [polyoxyethylene(15)] ammonium chloride with addition of 0.4 wt% amorphous silica

To the prepared solution of chromium (III) chloride hexahydrate salt in coco-alkylmethyl [polyoxyethylene(15)] ammonium chloride ionic liquid as described in Example 1 was added an amorphous silica aqueous colloidal solution which contained 8 wt% of active compound. The concentration of the amorphous silica in the prepared solution, expressed as the quantity of the active compound, was 4 g/kg.

About 250 ml of that solution was poured into the Hull cell described in Example 1. The cell was heated to a temperature of about 80°C.

The same pretreatment of the carbon steel substrate (cathode) as in Example 1 was performed, and again platinized titanium plate was applied as the anode. The potential difference was set to 30 V. The liquid was agitated using a centrally positioned top-entering impeller. The current flow between the electrodes was monitored on a meter connected in series.

After several hours of submission to the current, the cathode was disconnected from the power source and taken out of the cell. The plate was washed in water and acetone and then dried. Chemical analysis by scanning electron microscopy combined with X-ray dispersion (SEM/EDX) of the substrate confirmed deposition of chromium onto the carbon steel plate. The deposited layer thickness, measured using a thickness measurement device (Fischer, Germany) and by cross-cut metallographic analysis, was found to be ranging from 1 to 9 µm.

Example 4 – Electroplating of chromium from $CrCl_3$ hexahydrate salt onto carbon steel in coco alkyl methyl [polyoxyethylene(15)] ammonium chloride with addition of 1 wt% of carbon black

To the prepared solution of chromium (III) chloride hexahydrate salt in coco-alkylmethyl [polyoxyethylene(15)] ammonium chloride ionic liquid as described in Example 1 carbon black was added. The concentration of the carbon black in the prepared mixture was 10 g/kg.

About 250 ml of that mixture was poured into the Hull cell described in Example 1. The cell was heated to a temperature of about 70°C.

The same pretreatment of the carbon steel substrate (cathode) as in Example 1 was performed, and again platinized titanium plate was applied as the anode. The potential difference was set to 30 V. The liquid was agitated using a centrally positioned top-entering impeller. The current flow between the electrodes was monitored on a meter connected in series.

After several hours of submission to the current, the cathode was disconnected from the power source and taken out of the cell. The plate was washed in water and acetone and then dried. Chemical analysis by scanning electron microscopy combined with X-ray dispersion (SEM/EDX) of the substrate confirmed deposition of chromium onto the carbon steel plate. The deposited layer thickness, measured using a thickness measurement device (Fischer, Germany), was found to be ranging from 1 to 7 μm. The same thickness values were found by cross-cut metallographic analysis of the substrate samples.

CLAIMS

1. Use of an additive selected from the group consisting of amorphous silica, graphite powder, and a mixture thereof in a process to electroplate or electropolish a metal on a substrate using an ionic liquid as the electrolyte to increase metal layer thickness.

2. Use of the additive according to claim 1 wherein the ionic liquid is selected from the group consisting of $N^+R_1R_2R_3R_4\ X^-$, $N^+R_5R_6R_7R_8\ Y^-$, and mixtures thereof, wherein any one of R_1 to R_8 independently represents a hydrogen, alkyl, cycloalkyl, aryl, or aralkyl group that may be substituted with a group selected from OH, Cl, Br, F, I, phenyl, NH_2, CN, NO_2, $COOR_9$, CHO, COR_9, or OR_9, wherein at least one of R_1 to R_4 is an, optionally branched, fatty alkyl chain, wherein R_2 can be a (C_2-C_6 alkyl)-$N^+R_{16}R_{17}R_{18}$ group with R_{16}, R_{17}, R_{18} being similar to R_1, R_3, R_4, respectively, or a C_1 to C_4 alkyl chain, and wherein one or more of R_1 to R_8 can be a (poly)oxyalkylene group wherein the alkylene is a C_1 to C_4 alkylene and the total number of oxyalkylene units can be from 1 to 50 oxyalkylene units, and wherein at least one of R_1 to R_8 is a C_1 to C_4 alkyl chain, wherein R_9 is an alkyl or cycloalkyl group, wherein X^- is an anion compatible with the $N^+R_1R_2R_3R_4$ ammonium cation, such as a halogenide anion, a carboxylate anion, a sulphate (both organic and inorganic sulphate), sulphonate, carbonate, nitrate, nitrite, thiocyanate, hydroxide, saccharinate anion, or sulphonylimide anion, and wherein Y^- is an anion having a sulfonylimide anion or an N-acyl sulphonylimide anion ($-CO-N^--SO_2-$) functionality.

3. Use of the additive according to claim 1 or 2 wherein the metal which is electroplated or electropolished on the substrate originates from a metal source either being a metal salt selected from the group consisting of chromium, aluminium, titanium, zinc and copper salts, or an anode

selected from the group consisting of chromium, aluminium, titanium, zinc, and copper anodes.

4. Use of the additive according to any one of the preceding claims wherein the molar ratio of the cation of the ionic liquid to the metal cation of the metal salt or derived from the metal anode is between 1,000 : 1 and 3 :1, preferably between 100:1 and 7:1.

5. Use of the additive according to claim 4 in an amount of between 0.1 wt% and 5 wt%, based on the total weight of electrolyte.

6. Use of the additive according to any one of the preceding claims wherein the ionic liquid is selected from the group consisting of choline saccharinate, choline acesulphamate, hexadecyltrimethyl ammonium chloride, octadecyltrimethyl ammonium chloride, cocotrimethyl ammonium chloride, tallowtrimethyl ammonium chloride, hydrogenated tallowtrimethyl ammonium chloride, hydrogenated palmtrimethyl ammonium chloride, oleyltrimethyl ammonium chloride, soyatrimethyl ammonium chloride, cocobenzyldimethyl ammonium chloride, C_{12-16}-alkylbenzyldimethyl ammonium chloride, hydrogenated tallowbenzyldimethyl ammonium chloride, dioctyldimethyl ammonium chloride, didecyldimethyl ammonium chloride, dicocodimethyl ammonium nitrite, dicocodimethyl ammonium chloride, di(hydrogenated tallow)dimethyl ammonium chloride, di(hydrogenated tallow)benzylmethyl ammonium chloride, ditallowdimethyl ammonium chloride, dioctadecyldimethyl ammonium chloride, hydrogenated tallow(2-ethylhexyl)dimethyl ammonium chloride, hydrogenated tallow(2-ethylhexyl)dimethyl ammonium methylsulphate, trihexadecylmethyl ammonium chloride, octadecylmethylbis(2-hydroxyethyl) ammonium chloride, cocobis(2-hydroxyethyl)methyl ammonium nitrate, cocobis(2-hydroxyethyl)methyl ammonium chloride, cocobis(2-hydroxyethyl)benzyl ammonium chloride, oleylbis(2-hydroxyethyl)methyl

ammonium chloride, coco[polyoxyethylene(15)]methyl ammonium chloride, coco[polyoxyethylene(15)]methyl ammonium methylsulphate, coco[polyoxyethylene(17)]methyl ammonium chloride, octadecyl[polyoxyethylene(15)]methyl ammonium chloride, hydrogenated tallow[polyoxyethylene(15)]methyl ammonium chloride, tris(2-hydroxyethyl)tallow ammonium acetate, tallow-1,3-propane pentamethyl diammonium dichloride.

7. A method to electroplate or electropolish a metal on a metal substrate wherein an ionic liquid is selected from the group consisting of $N^+R_1R_2R_3R_4\,X^-$, $N^+R_5R_6R_7R_8\,Y^-$, and mixtures thereof, wherein any one of R_1 to R_8 independently represents a hydrogen, alkyl, cycloalkyl, aryl, or aralkyl group that may be substituted with a group selected from OH, Cl, Br, F, I, phenyl, NH_2, CN, NO_2, $COOR_9$, CHO, COR_9, or OR_9, wherein at least one of R_1 to R_4 is an, optionally branched, fatty alkyl chain, wherein R_2 can be a (C_2-C_6 alkyl)-$N^+R_{16}R_{17}R_{18}$ group with R_{16}, R_{17}, R_{18} being similar to R_1, R_3, R_4, respectively, or a C_1 to C_4 alkyl chain, and wherein one or more of R_1 to R_8 can be a (poly)oxyalkylene group wherein the alkylene is a C_1 to C_4 alkylene and the total number of oxyalkylene units can be from 1 to 50 oxyalkylene units, and wherein at least one of R_1 to R_8 is a C_1 to C_4 alkyl chain, wherein R_9 is an alkyl or cycloalkyl group, wherein X^- is an anion compatible with the $N^+R_1R_2R_3R_4$ ammonium cation, such as a halogenide anion, a carboxylate anion, a sulphate (both organic and inorganic sulphate), sulphonate, carbonate, nitrate, nitrite, thiocyanate, hydroxide, saccharinate anion, or sulphonylimide anion, and wherein Y^- is an anion having a sulfonylimide anion or an N-acyl sulphonylimide anion ($-CO-N^--SO_2-$) functionality; wherein a metal salt added to said ionic liquid or a metal anode is employed as metal source; and wherein said ionic liquid comprises at least 0.01 wt%, based on the total weight of electrolyte, of an additive selected from the group consisting of amorphous silica, graphite powder, and of a mixture thereof.

8. A method according to claim 7 wherein the metal which is electroplated or electropolished on the substrate originates from a metal source either being a metal salt selected from the group consisting of chromium, aluminium, titanium, zinc and copper salts, or an anode selected from the group consisting of chromium, aluminium, titanium, zinc, and copper anodes.

9. A method according to claim 7 or 8 wherein the molar ratio of the cation of the ionic liquid to the metal cation of the metal salt or derived from the metal anode is between 1,000 : 1 and 3 :1, and preferably between 100:1 and 7:1.

10. A method according to any one of claims 7-9 wherein the ionic liquid is selected from the group consisting of choline saccharinate, choline acesulphamate, hexadecyltrimethyl ammonium chloride, octadecyl-trimethyl ammonium chloride, cocotrimethyl ammonium chloride, tallowtrimethyl ammonium chloride, hydrogenated tallowtrimethyl ammonium chloride, hydrogenated palmtrimethyl ammonium chloride, oleyltrimethyl ammonium chloride, soyatrimethyl ammonium chloride, cocobenzyldimethyl ammonium chloride, C_{12-16}-alkylbenzyldimethyl ammonium chloride, hydrogenated tallowbenzyldimethyl ammonium chloride, dioctyldimethyl ammonium chloride, didecyldimethyl ammonium chloride, dicocodimethyl ammonium nitrite, dicocodimethyl ammonium chloride, di(hydrogenated tallow)dimethyl ammonium chloride, di(hydrogenated tallow)benzylmethyl ammonium chloride, ditallowdimethyl ammonium chloride, dioctadecyldimethyl ammonium chloride, hydrogenated tallow(2-ethylhexyl)dimethyl ammonium chloride, hydrogenated tallow(2-ethylhexyl)dimethyl ammonium methylsulphate, trihexadecylmethyl ammonium chloride, octadecylmethylbis(2-hydroxy-ethyl) ammonium chloride, cocobis(2-hydroxyethyl)methyl ammonium nitrate, cocobis(2-hydroxyethyl)methyl ammonium chloride, cocobis(2-

hydroxyethyl)benzyl ammonium chloride, oleylbis(2-hydroxyethyl)methyl ammonium chloride, coco[polyoxyethylene(15)]methyl ammonium chloride, coco[polyoxyethylene(15)]methyl ammonium methylsulphate, coco[polyoxyethylene(17)]methyl ammonium chloride, octadecyl[polyoxyethylene(15)]methyl ammonium chloride, hydrogenated tallow[polyoxyethylene(15)]methyl ammonium chloride, tris(2-hydroxyethyl)tallow ammonium acetate, tallow-1,3-propane pentamethyl diammonium dichloride.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2008/059962

A. CLASSIFICATION OF SUBJECT MATTER
INV. C25D3/66 C25D3/02 C25F3/16

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)
C25D C25F

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 practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2004/061919 A1 (TENCH D MORGAN [US] ET AL) 1 April 2004 (2004-04-01) paragraphs [0025], [0027] -----	1,7
A	US 2004/150866 A1 (TENCH D MORGAN [US] ET AL) 5 August 2004 (2004-08-05) paragraphs [0009], [0035] claim 16 ----- -/--	1,7

☒ 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 document but published on or after the international filing date

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

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

"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 November 2008	13/11/2008

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WANG P ET AL: "GELATION OF IONIC LIQUID-BASED ELECTROLYTES WITH SILICA NANOPARTICLES FOR QUASI-SOLID-STATE DYE-SENSITIZED SOLAR CELLS" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC, US, vol. 125, no. 5, 2003, pages 1166-1167, XP001172435 ISSN: 0002-7863 page 1166 -----	1,7

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2008/059962

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2004061919	A1	01-04-2004	NONE	
US 2004150866	A1	05-08-2004	NONE	