Electrochemical Deposition of Aluminum From Ionic Liquid Compositions

Ionic liquid composition comprising a dialkylamide compound of formula I wherein \( R_a \) and \( R_b \) are independently from each other a Cl-to C₆ alkyl group and \( m \) is an integral number from 4 to 18, an aluminum compound of formula II \( \text{Al}Y \), wherein \( Y \) is independently Cl, Br or F and an ionic liquid.
Electrochemical deposition of aluminum from ionic liquid compositions

Description

The invention relates to an ionic liquid composition comprising a dialkylamide compound of formula I

\[ \text{H}_3\text{C} - \left( \text{CH}_2 \right)_m \text{C} - \text{N} - \text{R}_a \text{O} - \text{R}_b \]

wherein \( \text{R}_a \) and \( \text{R}_b \) are independently from each other a \( \text{C}_1 \) to \( \text{C}_6 \) alkyl group and \( m \) is an integral number from 4 to 18,

an aluminum compound of formula II

\[ \text{AlY}_3 \]

wherein \( Y \) is independently \( \text{Cl} \), \( \text{Br} \) or \( \text{F} \)

and an ionic liquid.

This invention further relates to a process for the electrochemical deposition of aluminum and substrates with a coating of aluminum which are obtained by such process.

It is known that aluminum trihalides can be dissolved in ionic liquids to form aluminates and that processes for the deposition of aluminum can be performed using such solutions as electrolytes. Corresponding processes of aluminum deposition or aluminum plating are described, for example, in EP-A 339 536, EP-A 404188 and US 2012/0006688.

Aluminum coatings obtained by using electrolytes based on ionic liquids often have a poor appearance. In particular the aluminum coatings intend to have insufficient density and an irregular or rough surface. Often an undesired surface structure is observed known as dendrite formation. Moreover, high temperature is normally required in the electrodeposition process.

It has been tried to improve the appearance of the aluminum coatings by adding different additives (EP-A 404 188 and US 2012/0006688) or solvents (EP-A 339 536).

However, further improvement of the density and appearance of the aluminum coatings is desired.

Furthermore the process of electrochemical deposition should be easily performable, economically and effective.
Hence the process should allow high current densities, be performable at low temperatures and tolerate small water intake, for example from humidity or substrates to be coated.

Finally, the electrolyte and any components thereof should be non-toxic and non-flammable, and a good electrochemical stability of the ionic liquid against reduction and degradation in a wide range of potential is also required.

It is therefore an object of the invention to provide for an ionic liquid composition which is useful as electrolyte in electrochemical compositions of aluminum giving improved coating density and surface appearance and fulfills also the other requirements mentioned above.

We have accordingly found the ionic liquid composition and its use as electrolyte in electrochemical deposition of aluminum as defined in the outset.

To the dialkylamide

The ionic liquid composition comprises a dialkylamide compound of formula I

\[
\text{H}_3\text{C} - (\text{CH}_2)_{\text{m}}\text{C} = \text{N} - \text{R}_a \quad \text{R}_b
\]

wherein \( \text{R}_a \) and \( \text{R}_b \) are independently from each other a \( \text{C}1- \text{to C}6- \) alkyl group and \( \text{m} \) is an integral number from 4 to 18.

The dialkylamide of formula I is preferably a dialkylamide wherein \( \text{R}_a \) and \( \text{R}_b \) independently from each other are a \( \text{C}1- \text{to C}2- \) alkyl group. In a particularly preferred embodiments \( \text{R}_a \) and \( \text{R}_b \) are identical. Most preferred is a methyl group as \( \text{R}_a \) and \( \text{R}_b \).

Preferably \( \text{m} \) is an integral number from 4 to 12, particularly preferably \( \text{m} \) is 6, 8, 10 or 12.

As dialkylamide may be specifically mentioned:

- a dialkylamid with \( \text{m}=6 \), \( \text{R}_a \) = methyl and \( \text{R}_b \) = methyl (for short AMD8)
- a dialkylamid with \( \text{m}=8 \), \( \text{R}_a \) = methyl and \( \text{R}_b \) = methyl (for short AMD10)
- a dialkylamid with \( \text{m}=10 \), \( \text{R}_a \) = methyl and \( \text{R}_b \) = methyl (for short AMD12)
Such dialkylamides are available from BASF under the tradename Agnique® AMD.

To the aluminum compound

The ionic liquid composition further comprises an aluminum compound which is preferably aluminum trichloride, AlCl₃.

To the ionic liquid

The ionic liquid composition further comprises an ionic liquid.

The term ionic liquid refers to salts (compounds of cations and anions) which at atmospheric pressure (1 bar) have a melting point of less than 200°C, preferably less than 150°C, particularly preferably less than 100°C. Particularly preferred is an ionic liquid with a melting point below 20°C, respectively below 0°C.

The term ionic liquid as used herein also includes mixtures of different ionic liquids.

Preferred ionic liquids comprise an organic compound as cation (organic cation).

Suitable organic cations are, in particular, organic compounds having heteroatoms such as nitrogen, sulfur, oxygen or phosphorus; in particular, the organic cations are compounds having an ammonium group (ammonium cations), an oxonium group (oxonium cations), a sulfonium group (sulfonium cations) or a phosphonium group (phosphonium cations).

In a particular embodiment, the organic cations of the ionic liquids are ammonium cations, which for the present purposes are defined as

- nonaromatic compounds having a localized positive charge on the nitrogen atom, e.g. compounds having tetravalent nitrogen (quaternary ammonium compounds) or
- compounds having trivalent nitrogen, with one bond being a double bond, or
- aromatic compounds having a delocalized positive charge and at least one nitrogen atom, preferably from one to three nitrogen atoms, in the aromatic ring system.

Preference is given to organic cations which comprise a heterocyclic ring system having from one to three, in particular one or two, nitrogen atoms as constituents of the ring system.

Possible organic cations of this type are, for example, pyridinium cations, pyridazinium cations, pyrimidinium cations, pyrazinium cations, imidazolium cations, pyrazolium cations, pyrazolinium cations, imidazolinium cations, thiazolium cations, triazolium cations, pyrrolidinium cations and imidazolidinium cations. These cations are described, for example, in WO 2005/1 13702. Insofar as it is necessary for a positive charge on the nitrogen atom or in the aromatic ring system, the nitrogen atoms are in each case substituted by a hydrogen atom or an organic group which
generally has not more than 20 carbon atoms, preferably a hydrocarbon group, in particular a C1-C16-alkyl group, in particular a C1-C10-alkyl group, particularly preferably a C1-C4-alkyl group.

The carbon atoms of the ring system can also be substituted by organic groups which generally have not more than 20 carbon atoms, preferably a hydrocarbon group, in particular a C1- to C16-alkyl group, in particular a C1- to C10-alkyl group, particularly preferably a C1- to C4-alkyl group.

Particular preference is given to ionic liquids with an imidazolium cation.

The ionic liquids can comprise inorganic or organic anions.

As possible anions may be mentioned:

alkylsulfates
\[ R^n\text{OSO}_3^- \]
where \( R^n \) is a C1-C12-alkyl group or a C5-C12-aryl group, preferably a C1-C6-alkyl group or a C6-aryl group (tosylate),

alkylsulfonates
\[ R^n\text{SO}_3^- \]
where \( R^n \) is a C1-C12-alkyl group, preferably a C1-C6-alkyl group,

halides, in particular chloride, bromide or iodide, and pseudohalides such as thiocyanate, dicyanamide,

carboxylates \[ R^n\text{COO}^- \]
where \( R^n \) is a C1- to C20-alkyl group, preferably a C1- to C8-alkyl group, in particular acetate, phosphates, in particular the dialkyl phosphates of the formula \( R^aR^b\text{P04}^- \), where \( R^a \) and \( R^b \) are each, independently of one another, a C1-C6-alkyl group; in particular, \( R^a \) and \( R^b \) are the same alkyl group, with mention being able to be made of dimethyl phosphate and diethyl phosphate, and phosphonates, in particular monoalkyl phosphonates of the formula \( R^aR^b\text{P03}^- \), where \( R^a \) and \( R^b \) are each, independently of one another, a C1-C6-alkyl group.

Preferred anions are halides, in particular chloride, bromide or iodide; very particular preference is given to chloride as anion in the ionic liquids.
The ionic liquid is particularly preferably an imidazolium salt of the formula III below,

\[
\begin{array}{c}
\text{R5} \\
\text{R4} \\
\text{N} \\
\text{N} \\
\text{R1} \\
\text{R3} \\
\text{R2} \\
\end{array}
\]

where

- \( R_1 \) is an organic radical having from 1 to 20 carbon atoms,
- \( R_2, R_4, R_3 \) and \( R_5 \) are each an \( H \) atom or an organic radical having from 1 to 20 carbon atoms,
- \( X \) is an anion and
- \( n \) is 1, 2 or 3.

In formula III, preference is given to \( R_1 \) and \( R_3 \) each being, independently of one another, an organic radical having from 1 to 10 carbon atoms. In particular, \( R_1 \) and \( R_3 \) are each an aliphatic radical, in particular an aliphatic radical without further heteroatoms, e.g. an alkyl group. Particular preference is given to \( R_1 \) and \( R_3 \) each being, independently of one another, a \( C_1 \)-to-\( C_{10} \)-alkyl group or a \( C_1 \)-to-\( C_{4} \)-alkyl group.

In formula III, preference is given to \( R_2, R_4 \) and \( R_5 \) each being, independently of one another, an \( H \) atom or an organic radical having from 1 to 10 carbon atoms; in particular, \( R_2, R_4 \) and \( R_5 \) are each an \( H \) atom or an aliphatic radical. Particular preference is given to \( R_2, R_4 \) and \( R_5 \) each being, independently of one another, an \( H \) atom or an alkyl group; in particular, \( R_2, R_4 \) and \( R_5 \) are each, independently of one another, an \( H \) atom or a \( C_1 \)-to-\( C_{4} \)-alkyl group. Very particular preference is given to \( R_2, R_4 \) and \( R_5 \) each being an \( H \) atom.

- \( n \) is preferably 1.

- \( X \) is preferably one of the abovementioned preferred anions; \( X \) is particularly preferably a halide and very particularly preferably a chloride.

Suitable ionic liquids may be obtained under the trade name Baisonics® from BASF.
To the ionic liquid composition

In the following the term "ionic liquid" shall refer to the ionic liquid defined above which is used as starting material, if not mentioned otherwise or obvious from the context.

In the ionic liquid composition various salts are formed from the above ionic liquid, dialkylamide and aluminum compound.

Aluminum trihalides and the above ionic liquid form aluminates, for example tetrahaloaluminates. Thus the ionic liquid composition comprises a new anion to the ionic liquid. The anion X (see formula III) to the ionic liquid is replaced partially or totally by an aluminate formed from the anion X and the aluminum trihalide.

In case of the preferred imidazolium chloride and aluminum trichloride the anion formed is an aluminate of general formula \( (\text{AlCl}_3\text{X}+) \), preferably \( \text{AlCl}_4^- \) or \( \text{Al}_2\text{Cl}_7^- \) and particularly a mixture thereof.

The dialkylamide of formula I may also react with the aluminum trihalide and thus take part in salt formation.

For the definition of the contents of the above ionic liquid, dialkylamide and aluminum compound (starting materials) in the ionic liquid composition we refer to the amounts in which these starting materials are added to the ionic liquid composition. When using the word "comprising" we refer to the amounts of components added as well, knowing, that in fact the ionic liquid composition finally comprises not or not only the components as such, but salts formed thereof.

The ionic liquid composition preferably comprises certain molar ratios of the above components. For defining these molar ratios the content of ionic liquid (preferably imidazolium chloride) and dialkylamide is added and set in relation to the aluminum compound (preferably aluminum trichloride).

The ionic liquid composition preferably comprises 1.2 to 3 mol aluminum compound, more preferably 1.2 to 2.5 mol aluminum compound, most preferably 1.2 to 1.8 mol aluminum compound and in particular 1.5 to 1.8 mol aluminum compound, based on one 1 mol of the sum of ionic liquid and dialkylamide.

The stoichiometric ratio of ionic liquid and dialkylamide to the aluminum compound determines the composition of the aluminates.

The content of the dialkylamide may be further defined by the parts by weight of dialkylamide in relation to the parts by weight of the sum of ionic liquid and aluminum compound.
On 100 parts by weight of the sum of ionic liquid and aluminum compound, the ionic liquid composition comprises
preferably 1 to 200 parts by weight of dialkylamide,
more preferably 5 to 100 parts by weight of dialkylamide,
most preferably 10 to 50 parts by weight of dialkylamide and
in a particularly preferred embodiment 10 to 30 parts by weight of dialkylamide.

In a particularly preferred embodiment of the invention, the ionic liquid composition comprises
an imidazolium chloride of formula III, aluminum trichloride and a dialkylamide of formula I in the
forestanding preferred amounts.

The ionic liquid composition of this invention may be formed from the above components by any
means or in any sequence of addition, for example the aluminum trihalide (preferably aluminum trichloride) and the dialkylamide may be added to the ionic liquid.

The ionic liquid composition of this invention is obtainable by forming a composition from the
dialkylamide of formula I, the aluminum compound of formula II and the ionic liquid (preferably
an imidazolium salt according to formula III, most preferred an imidazolium chloride) in the
amounts and ratios disclosed above.

The ionic liquid composition may comprise further components.
For example the ionic liquid composition may comprise additives as mentioned in EP-A 404 188
The organic solvent may be selected, for example, from the group of aromatics and heteroaromatics and can preferably be toluene, chlorobenzene, 1,2-dichlorobenzene, 1,3-
dichlorobenzene, 1,3-dichlorobenzene, trichlorobenzene or xylene.
The ionic liquid composition may comprise, for example, from 0 to 10% by weight of additives and from 0 to 50% by weight, in particular from 0 to 30% by weight, of organic solvents.

The ionic liquid composition may comprise further additives used in electrochemical processes.

Water is known to have a negative impact on electrochemical deposition of aluminum. Hence
the water content of the ionic liquid composition should be low.
Preferably the ionic liquid composition comprises less than 2 parts by weight of water, in par-
ticular less than 0.2 parts by weight of water, preferably less than 0.05 most preferred less than
0.01 parts by weight of water on 100 parts by weight of the total ionic liquid composition. In a
most preferred embodiment the ionic liquid composition comprises essentially no water.

In a preferred embodiment the ionic liquid composition is to at least 60% by weight, more prefer-
erably to at least 80% by weight, most preferably to at least 90% by weight and particularly preferred to at least 95% by weight composed of the starting materials ionic liquid, aluminum com-
pound and dialkylamide and salts formed thereof, only.
The ionic liquid composition of this invention may be used as electrolyte.

In particular the ionic liquid composition may be used in a process for the electrochemical deposition of aluminum. In such process the ionic liquid composition is used as electrolyte and aluminum is deposited from such electrolyte on a substrate, which preferably serves as cathode.

In processes for the electrochemical deposition of aluminum, usually an electrolysis apparatus having at least one anode and at least one cathode in an electrolysis cell is used. The anode and the cathode are electrolytically conductively connected by the electrolyte which is the ionic liquid composition of the invention.

It is possible to use one anode, but it is also possible to use a plurality of anodes. In case of a plurality of anodes, the anodes may be identical or may be different. The same applies to the cathode(s). The singular will be used in the following, but what is said also applies analogously in each case to embodiments having a plurality of anodes and/or cathodes.

The anode may comprise, for example, aluminum or platinum. Preferably the anode comprises aluminum. Aluminum comprising anodes often are also referred to as sacrificial anode.

The anode preferably comprises aluminum in a proportion by weight of at least 95% by weight, preferably 99% by weight, more preferably at least 99.5% by weight, based on the total weight of the anode.

The cathode arranged in the electrolysis apparatus can be selected from various conductive materials, e.g. metals, metal alloys, graphite, electrically conductive plastics or polymers and steels. In particular, the material of the cathode is selected from metals, alloys and steels, and is particularly preferably selected from steel, Ni alloys, Cu alloys, Zn alloys and Al alloys.

Electrodeposition of aluminum could be realized on different metals or composites and electrically conductive materials. Various metals or electrically conductive materials could be used as counter electrode (cathode).

In a preferred embodiment a copper rod is used as cathode (WE, working electrode) and an aluminum rod is used as anode (CE = counter electrode).

In the electrochemical deposition of aluminum, the article to be coated preferably serves as cathode on which the aluminum deposits.

In a preferred embodiment of the invention, the cathode is a workpiece on which aluminum is deposited. Such deposits of aluminum may for example be for decorative purposes or to impart anticorrosion properties to the workpiece.
The process of electrochemical deposition may, for example, be performed at a temperature of the electrolyte in the range from 20 to 200°C, preferably at a temperature in the range from 20 to 120°C, particularly preferably at a temperature in the range from 20 to 90°C. It is advantage of the instant invention that the process can be performed successfully at low temperatures, in particular at temperatures of at maximum 80°C, for example at temperature from 20 to 80°C, respectively 25 to 60°C.

The absolute value of the reduction current density at which the coating process is carried out can vary over a wide range; in particular, it is at least 20 Ampere (A) /m². The electric current density is defined as the ratio of current to effective electrode area in the electrolysis. The electric current density is preferably at least 50 A/m², more preferably at least 100 A/m². Generally, the current density is not higher than 1000, in particular 500 A/m².

Typically, a current density of - 50 A/m² is applied with pulses of 80 ms (milliseconds) separated by relaxation period of 20 ms. Electrodeposition is realized at room temperature (25°C) under constant stirring of 300 rpm, and in inert conditions under argon atmosphere. Grey metallic and adherent deposits are achieved following this specific method after 5 minutes of pulsed of applied current. The sequence can be repeated in order to obtain the desired thickness.

Electrodeposition of metals through the ionic liquid composition of the invention could be achieved following different methods as constant potential, current applied or cyclic voltammetry. More preferably constant current method is applied for economical and feasibility reasons. More preferably, pulsed techniques are used in the final aim to limit the active-species depreciation at the surface of the electrode and ensuring a homogeneous coating.

Other techniques not detailed in this patent could be also used to realize the deposition of aluminum.

The ionic liquid compositions of the invention have a variety of advantages. They are suitable electrolytes for the electrochemical deposition of aluminum. The aluminum depositions obtained by the process have a high density, are uniform and have a very good optical appearance. The deposition process can be performed at high current densities and at low temperatures. The dialkylamide which forms part of the ionic liquid composition is non-toxic and non-flammable. The stability of the ionic liquid composition is neatly improved by the addition of the dialkylamide.

The mixture of ionic liquid and the dialkylamide has a lower reduction potential than the ionic liquid as such. For example, a delay of approximately 1 V for the degradation of the new ionic liquid is observed in comparison with the same mixture without the dialkylamide (see figure 1, with reduction caused by degradation of the electrolyte at about -2 V in curve a and reduction art about -3 V in curve b).
Furthermore the dialkylamide imparts hydrophobicity to the ionic liquid composition which results in less water-intake into the composition as well as a better performance in the presence of low amounts of water in the composition (higher water tolerance).

Examples

Materials

The following materials have been used in the examples:

Dialkylamides
AMD8: which is a dialkylamid of formula I with m=6, Rₐ and Rₐ=methyl
AMD1 0: which is a dialkylamid of formula I with m=8, Rₐ and Rₐ=methyl
AMD1 2: which is a dialkylamid of formula I with m=10, Rₐ and Rₐ=methyl

The dialkylamides have been obtained from BASF.

Ionic Liquids
EMIM chloride: which is 1-Ethyl-3-methyl-imidazolium chloride (see formula III, with R1=ethyl and R3=methyl)

Aluminum trichloride was from Sigma - Aldrich.

Ionic liquid compositions

Precursors and drying procedure
Solution of 1-Ethyl-3-methylimidazolium tetrachloroaluminate (EMIM·MCl₄, Sigma Aldrich ref. 51059, CAS 80432-05-9, BASF quality, > 95%), Powder of aluminum chloride (AlCl₃, Sigma Aldrich ref. 06220, CAS 7446-70-0, Fluka puriss. p.a., anhydrous, crystallized, > 99.0% (AT)), 1 Ethyl-3-methylimidazolium chloride (EMIM·MCl, BASF, CAS 65039-09-0, Basionics ST 80) have been used as received without more purification steps. EMIM·MCl has been melt and dried under vacuum (800°C, 7 mbar, 24 hours) and placed inside the pre-chamber of the glove box to be cooled (liquid → solid) under vacuum overnight prior to be used. Bottles of 200 ml of dimethylamide green solvent (Agnique AMD8, AMD1 0 and AMD1 2) have been dried with 50 g molecular sieve per bottle (Sigma Aldrich, ref. 208590-1 kg, CAS 70955-01-0, 4Å beads, 4 - 8 mesh). Water content in AMD 8, AMD 10 and AMD 12 after drying; 0.01%, 0.03% and 0.02% respectively.

The ionic liquid compositions have been prepared inside a glove box in inert conditions. In the first step the powder of EMIM·MCl (Basionics ST 80), has been melt at 80°C and kept under vigorous stirring for the addition of AlCl₃ powder. Due to the very exothermic reaction, at the beginning AlCl₃ was added very progressively. When the ratio AlCl₃ : EMIM·MCl was approximately 1:1, the powder could be added faster.
Dimethylamide was added to the previous preparation at room temperature under stirring. The addition was exothermic and temperature increases from room temperature 20-25°C up to approximately to 40 - 70°C depending on the solvent and quantity used.

Details on the ionic liquid composition are obvious from Table 1:

<table>
<thead>
<tr>
<th>Composition</th>
<th>Dialkylamide</th>
<th>Dialkylamide (mmol)</th>
<th>Ionic liquid (IL) (mmol)</th>
<th>AlCl3 (mmol)</th>
<th>Molar ratio AlCl3 to (IL + AMD)</th>
<th>Volume % Dialkylamide in composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>LI-201/10</td>
<td>AMD8</td>
<td>10,82</td>
<td>85,98</td>
<td>125,49</td>
<td>1,30</td>
<td>10</td>
</tr>
<tr>
<td>LI-201/11</td>
<td>AMD8</td>
<td>21,65</td>
<td>76,42</td>
<td>111,55</td>
<td>1,14</td>
<td>20</td>
</tr>
<tr>
<td>LI-201/12</td>
<td>AMD8</td>
<td>32,47</td>
<td>66,87</td>
<td>97,60</td>
<td>0,98</td>
<td>30</td>
</tr>
<tr>
<td>LI-201/17</td>
<td>AMD8</td>
<td>10,82</td>
<td>74,07</td>
<td>148,13</td>
<td>1,74</td>
<td>10</td>
</tr>
<tr>
<td>LI-201/18</td>
<td>AMD8</td>
<td>21,65</td>
<td>65,88</td>
<td>131,70</td>
<td>1,50</td>
<td>20</td>
</tr>
<tr>
<td>LI-201/19</td>
<td>AMD8</td>
<td>32,47</td>
<td>57,63</td>
<td>115,28</td>
<td>1,28</td>
<td>30</td>
</tr>
<tr>
<td>LI-201/20</td>
<td>AMD8</td>
<td>43,30</td>
<td>49,38</td>
<td>98,78</td>
<td>1,07</td>
<td>40</td>
</tr>
<tr>
<td>LI-201/21</td>
<td>AMD10</td>
<td>8,80</td>
<td>83,41</td>
<td>125,33</td>
<td>1,36</td>
<td>20</td>
</tr>
<tr>
<td>LI-201/22</td>
<td>AMD10</td>
<td>17,61</td>
<td>74,14</td>
<td>111,38</td>
<td>1,21</td>
<td>20</td>
</tr>
<tr>
<td>LI-201/23</td>
<td>AMD10</td>
<td>26,41</td>
<td>64,93</td>
<td>97,43</td>
<td>1,07</td>
<td>30</td>
</tr>
<tr>
<td>LI-201/24</td>
<td>AMD12</td>
<td>7,89</td>
<td>83,41</td>
<td>125,33</td>
<td>1,37</td>
<td>10</td>
</tr>
<tr>
<td>LI-201/25</td>
<td>AMD12</td>
<td>15,78</td>
<td>74,14</td>
<td>111,38</td>
<td>1,24</td>
<td>20</td>
</tr>
<tr>
<td>LI-201/26</td>
<td>AMD12</td>
<td>23,67</td>
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<td>97,43</td>
<td>1,10</td>
<td>30</td>
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<tr>
<td>LI-201/27</td>
<td>AMD12</td>
<td>31,56</td>
<td>49,38</td>
<td>98,78</td>
<td>1,22</td>
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<tr>
<td>LI-201/28</td>
<td>AMD12</td>
<td>127,41</td>
<td>115,67</td>
<td>306,38</td>
<td>1,26</td>
<td>50</td>
</tr>
</tbody>
</table>

Electrochemical characteristics:

The ionic liquid compositions obtained above have been characterized by cyclic voltammetry. Results are summarized in Table 2. Determination has been done at room temperature, 25°C, in a 3 electrode cell.

The working electrode (WE) was a platinum (PT) electrode. The counter electrode (CE) was a platinum (PT) electrode. As reference electrode a Ag/Ag+ (tetra butyl ammonium perchlorate 0.1 molar in acetonitrile) electrode was used.

All potentials have been normalized to the normal hydrogen electrode as reference electrode in order to be able to compare the values with standard values in literature.
The ionic liquid compositions were used as electrolyte.

The current is measured and plotted against the potential of the WE with a scan rate of 25 mV/second. Results are shown in table 2 and figure 1.

In table 2 below the potential in volt (V) and current density in mA/cm² at the first reduction of the electrolyte are listed.

<table>
<thead>
<tr>
<th>Composition</th>
<th>AMD type</th>
<th>AMD Volume %</th>
<th>molar ratio AlCl₃ to (IL+AMD)</th>
<th>1st Reduction (V)</th>
<th>1st Reduction (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LI-201/17</td>
<td>AMD8</td>
<td>10%</td>
<td>1.74</td>
<td>-1,377</td>
<td>-30,42</td>
</tr>
<tr>
<td>LI-201/8(2)</td>
<td>No</td>
<td>0%</td>
<td>1.46</td>
<td>-1,32</td>
<td>-29,15</td>
</tr>
<tr>
<td>LI-201/7(3)</td>
<td>No</td>
<td>0%</td>
<td>1.53</td>
<td>-1,37</td>
<td>-29,15</td>
</tr>
<tr>
<td>LI-201/24</td>
<td>AMD12</td>
<td>10%</td>
<td>1.37</td>
<td>-1,832</td>
<td>-18,42</td>
</tr>
<tr>
<td>LI-201/10</td>
<td>AMD8</td>
<td>10%</td>
<td>1.3</td>
<td>-1,25</td>
<td>-15,6</td>
</tr>
<tr>
<td>LI-201/21</td>
<td>AMD10</td>
<td>10%</td>
<td>1.36</td>
<td>-1,18</td>
<td>-14,77</td>
</tr>
<tr>
<td>LI-201/18</td>
<td>AMD8</td>
<td>20%</td>
<td>1.5</td>
<td>-1,254</td>
<td>-13</td>
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<td>AMD8</td>
<td>30%</td>
<td>1.28</td>
<td>-1,193</td>
<td>-8,71</td>
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<td>LI-201/25</td>
<td>AMD12</td>
<td>20%</td>
<td>1.24</td>
<td>-1,359</td>
<td>-8,14</td>
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<td>LI-201/28</td>
<td>AMD12</td>
<td>50%</td>
<td>1.26</td>
<td>-1,557</td>
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<td>LI-201/22</td>
<td>AMD10</td>
<td>20%</td>
<td>1.21</td>
<td>-1,229</td>
<td>-6,71</td>
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<td>LI-201/11</td>
<td>AMD8</td>
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<td>1.14</td>
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<td>AMD8</td>
<td>30%</td>
<td>0.98</td>
<td>-1,62</td>
<td>-0,91</td>
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<td>LI-201/20</td>
<td>AMD8</td>
<td>40%</td>
<td>1.07</td>
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<td>LI-201/23</td>
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<td>-0,62</td>
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<tr>
<td>LI-201/26</td>
<td>AMD12</td>
<td>30%</td>
<td>1.1</td>
<td>-1,663</td>
<td>-0,49</td>
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</table>

The ionic liquid compositions containing dialkylamide and in particular dimethylamide, show a much better reduction stability, more cathodic stability in comparison with ionic liquids without these dialkylamides, as it is shown in Fig. 1 as example. Composition LI-201/8(2) without the dialkylamide shows a reduction around -2 V (figure 1, curve a) while the ionic liquid containing 10% AMD 8 (LI-201/10) has a reduction at approximately -3 V (figure 1 curve b). This is a general behavior in the new ionic liquids described in the present invention.
Figure 1 is a cyclic voltammogram of the following ionic liquid compositions:

- LI-201/8(2) without AMD: curve a
- LI-201/10 with 10% AMD8: curve b
- LI-201/11 with 20% AMD8: curve c
- LI-201/12) with 30% AMD8: curve d

Performance of the electrochemical deposition

Copper rod (0.6 mm, Farnell, Ref. 709-6963) has been used as working electrodes (WE). Aluminum rod (0.127 mm, Farnell, Ref. 681-053, configuration has been used as counter electrode (CE).

Prior to use the surface of the electrode has been polished until a mirror polishing. Rods of copper have been cut and successively polished from 320 to 4000 grade emery paper, 1 µη and 0.5 µη alumina suspension.

Electrochemical deposition has been processing by galvanostatic (constant current density). The current density was -5 mA/cm² and has been applied with pulses of 80 ms separated by relaxation period of 20 ms, during 5 or 10 minutes. The electrodeposition has been realized at room temperature (25°C) under a constant stirring of 300 rpm and in inert conditions in a globe box, under argon atmosphere. Results are summarized in Table 3.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Dialkylamide</th>
<th>molar ratio AI CI3 to (IL+AMD)</th>
<th>AMD Volume % in composition</th>
<th>Time (min)</th>
<th>Deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td>LI-201/11</td>
<td>AMD8</td>
<td>1.14</td>
<td>20%</td>
<td>10</td>
<td>No</td>
</tr>
<tr>
<td>LI-201/12</td>
<td>AMD8</td>
<td>0.98</td>
<td>30%</td>
<td>10</td>
<td>No</td>
</tr>
<tr>
<td>LI-201/20</td>
<td>AMD8</td>
<td>1.07</td>
<td>40%</td>
<td>5</td>
<td>No</td>
</tr>
<tr>
<td>LI-201/23</td>
<td>AMD10</td>
<td>1.07</td>
<td>30%</td>
<td>5</td>
<td>No</td>
</tr>
<tr>
<td>LI-201/26</td>
<td>AMD12</td>
<td>1.1</td>
<td>30%</td>
<td>5</td>
<td>No</td>
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<tr>
<td>LI-201/10</td>
<td>AMD8</td>
<td>1.3</td>
<td>10%</td>
<td>10</td>
<td>Very good, uniform deposit</td>
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<tr>
<td>LI-201/17</td>
<td>AMD8</td>
<td>1.74</td>
<td>10%</td>
<td>5</td>
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</tr>
<tr>
<td>LI-201/18</td>
<td>AMD8</td>
<td>1.5</td>
<td>20%</td>
<td>5</td>
<td>Very good, uniform deposit</td>
</tr>
<tr>
<td>LI-201/19</td>
<td>AMD8</td>
<td>1.28</td>
<td>30%</td>
<td>5</td>
<td>Very good, uniform deposit</td>
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<tr>
<td>LI-201/21</td>
<td>AMD10</td>
<td>1.36</td>
<td>10%</td>
<td>5</td>
<td>Very good, uniform deposit</td>
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<td>LI-201/22</td>
<td>AMD10</td>
<td>1.21</td>
<td>20%</td>
<td>5</td>
<td>Very good, uniform deposit</td>
</tr>
<tr>
<td>LI-201/24</td>
<td>AMD12</td>
<td>1.37</td>
<td>10%</td>
<td>5</td>
<td>Very good, uniform deposit</td>
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<td>LI-201/25</td>
<td>AMD12</td>
<td>1.24</td>
<td>20%</td>
<td>5</td>
<td>Very good, uniform deposit</td>
</tr>
</tbody>
</table>
### Table 1: Composition, Dialkylamide, molar ratio, AMD, Volume % in composition, Time, Deposit

<table>
<thead>
<tr>
<th>Composition</th>
<th>Dialkylamide</th>
<th>molar ratio AlCl3 to (IL+AMD)</th>
<th>AMD</th>
<th>Time (min)</th>
<th>Deposit</th>
</tr>
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<tbody>
<tr>
<td>LI-201/27</td>
<td>AMD12</td>
<td>1.22</td>
<td>38%</td>
<td>5</td>
<td>Very good, uniform deposit</td>
</tr>
<tr>
<td>LI-201/28</td>
<td>AMD12</td>
<td>1.26</td>
<td>50%</td>
<td>5</td>
<td>Very good, uniform deposit</td>
</tr>
<tr>
<td>LI-201/8(2)</td>
<td>no</td>
<td>1.5</td>
<td>0%</td>
<td>10</td>
<td>Not acceptable, irregular surface</td>
</tr>
<tr>
<td>LI-201/7(3)</td>
<td>no</td>
<td>1.5</td>
<td>0%</td>
<td>10</td>
<td>Not acceptable, irregular surface</td>
</tr>
</tbody>
</table>

Working in the same conditions better Al deposit is obtained with the ionic liquid containing dialkylamides in their composition. Thus, as example composition LI-201/10, LI-201/24 and LI-201/25, show a more uniform, adherent and shining uniform metallic deposit of Al in comparison with composition without dialkylamide LI-201/8, in which no good Al electrodeposition was achieved working at room temperature in the same conditions (Fig 2 and Fig 3).
1. Ionic liquid composition comprising a dialkylamide compound of formula I

\[
\begin{align*}
\text{H}_3\text{C} & \left( \text{CH}_2 \right)_m \text{O} \text{C} \text{N} \text{R}_a \\
& \quad \text{N} \text{R}_b
\end{align*}
\]

wherein \( \text{R}_a \) and \( \text{R}_b \) are independently from each other a C1- to C6- alkyl group and \( m \) is an integral number from 4 to 18.

2. The ionic liquid composition according to claim 1, wherein the dialkylamide of formula I is a compound wherein \( \text{R}_a \) and \( \text{R}_b \) independently from each other are a C1- or (C2-) alkyl group and \( m \) is an integral number from 4 to 12.

3. The ionic liquid composition according to claim 1 or 2, wherein the aluminum compound of formula II is aluminum trichloride.

4. The ionic liquid composition according to any of claims 1 to 3, wherein the ionic liquid is an imidazolium salt of formula III

\[
\begin{bmatrix}
\text{R}_4 \quad \text{R}_5 \\
\text{R}_3 \\
\text{R}_2 \quad \text{R}_1
\end{bmatrix}^n \quad X^{-}
\]

wherein

\( \text{R}_1 \) is an organic radical having from 1 to 20 carbon atoms,
R2, R3, R4 and R5 are each an H atom or an organic radical having from 1 to 20 carbon atoms,
X is an anion and
n is 1, 2 or 3.

5. The ionic liquid composition according to any of claims 1 to 4, wherein the ionic liquid is an imidazolium salt of formula III wherein R1 and R3 independently of one another are a C1- to C10-alkyl group, n is 1 and the anion X is a chloride.

6. The ionic liquid composition according to any of claims 1 to 5, wherein the molar ratio of the aluminum compound to the sum of the ionic liquid and the dialkylamide in the ionic liquid composition is from 1.2 to 1 up to 3 to 1.

7. The ionic liquid composition according to any of claims 1 to 6, wherein the ionic liquid composition comprises 1 to 200 parts by weight of dialkylamide on 100 parts by weight of the total sum of ionic liquid and aluminum compound.

8. The ionic liquid composition according to any of claims 1 to 7, wherein the ionic liquid composition comprises 10 to 50 parts by weight of dialkylamide on 100 parts by weight of the total sum of ionic liquid and aluminum compound.

9. Ionic liquid composition obtainable by forming a composition from the dialkylamide of formula I, the aluminum compound of formula II and the ionic liquid

10. Use of the ionic liquid composition according to any of claims 1 to 9 as electrolyte.

11. A process for the electrochemical deposition of aluminum, wherein the ionic liquid composition according to any of claims 1 to 9 is used as electrolyte and aluminum is deposited from such electrolyte on a substrate serving as cathode.

12. A process according to claim 11, wherein the electrolyte is kept at a temperature of at maximum 80°C.

13. Substrates with a coating of aluminum and obtained by the use according to claim 10 or the process according to claim 11 or 12.
Figure 1: cyclic voltammetry of ionic liquid compositions
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**


ADD.

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

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C25D

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, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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Further documents are listed in the continuation of Box C.

See patent family annex.

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  **E** earlier application or patent but published on or after the international filing date
  
  **L** document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  
  **O** document referring to an oral disclosure, use, exhibition or other means
  
  **P** document published prior to the international filing date but later than the priority date claimed

**Date of the actual completion of the international search**

31 October 2014

**Date of mailing of the international search report**

10/11/2014

**Name and mailing address of the ISA**

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

Authorized officer

Suarez Ramon, C
## DOCUMENTS CONSIDERED TO BE RELEVANT

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