Electrodeposition of Aluminum on Cathodes in Ionic Liquid Based Choline Chloride/Urea/ALCL₃

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Received: June 21, 2014   Accepted: July 30, 2014   Online Published: September 24, 2014
doi:10.5539/ep.v3n4p59          URL: http://dx.doi.org/10.5539/ep.v3n4p59

Abstract

Electrodeposition of aluminum on metal at low temperatures, with the participation of the ionic liquid electrolyte will contribute to solving many technical issues in critical industries such as automobiles, aircraft, electronics ... the industry uses aluminum and aluminum coated materials most. Using ionic liquids based on choline chloride and urea to electrodeposition of aluminum is more published in scientific journals in the world. In this article, we present the preliminary results of electrodeposition of aluminum on cathodes as copper, iron and especially glassy carbon. The nature of electrolytes based on choline chloride and urea were analyzed and identified. The solubility of aluminum chloride in this mixture also surveyed. The results showed that only choline chloride mixture / urea with a mole ratio of 1:1 solution is to create transparent and recrystallized at room temperature. The nature of electrolytes based on choline chloride and urea were analyzed and identified. The solubility of aluminum chloride in this mixture also surveyed. The results showed that only choline chloride mixture / urea with a mole ratio of 1:1 solution is to create transparent and recrystallized at room temperature. Solubility of aluminum chloride in this system is 5% by weight. So in the study of aluminum deposited on the cathode, we use only liquid choline chloride / urea / AlCl₃ at the rate of 1 mol / 1 mol + 5% by weight of AlCl₃. The electroplating are made with temperatures from 90-120 °C, the time is 2 hours. Distance between two poles is 2 cm, the maximum of surface area 3 cm² voltage between the two poles from 1-3 V and amperage stable at 100 - 150 mA. Nitrogen environment are set to limit the influence of oxygen and hydrogen. The results of the analysis on the cathode structure of aluminum films by XRD, SEM, XRF, EDS ... showed similarities with the aluminum anode. The purity of the aluminum film obtained depending on the materials used as the cathode. The purity of aluminum on the GC-cathode is 92.42 % atom, on iron is 70.33 % atom and on copper is 82.63 % atom.

Keywords: electrodeposition, aluminum, deep eutectic solvent (DES), ionic liquid, conductivity

1. Introduction

Research using ionic liquids for electrodepositing of aluminum was Hurley FH and Wier TP, published in 1951 [Hurley F. H., Wier T. P.]. Accordingly, the authors have proposed the use of low-temperature molten salt, formed by the combination of aluminum chloride anhydrous salt with organic compounds such as 1-ethyl-3-methylimidazolium chloride [EMim]Cl as the electrolyte for aluminum electroplating process at low temperatures. Ionic liquids based on AlCl₃, can be considered as the first generation of ionic liquids. The ionic liquid has the advantage over the previous generation using ionic liquids as Tetrafluoroborate anion [BF₄]⁻ or hexafluorophotphat [PF₆]⁻ hydrophobic by nature and their stability. In addition, during electrodeposition do not appear toxic HF gas for environmental.

Over the past 10 years, the research in this direction is special attention. The difference is the use of ionic liquids recently quite diverse, such as EMIM [Tf2N]-AlCl₃, Trimethylphenylammonium chloride (TMPAC), EMIM) Br, J. L. Solá Cervera and A. König, Liu Q. et al, Brown L., Li-peng Zhang et al, S. Zein El Abedin et al, F. Endres] or mixed system between 1-butyl-1-methylpyrrolidinium chloride/AlCl₃ and 1-ethyl-3-methylimidazolium chloride/AlCl₃ [Giridhar P, et al, S. Zein El Abedin et al]. 1-Butyl-1-sulfonate-ethylpyrrolidiniumtrifluoromethyl [Giridhar P. et al], piperidinum-Alkyl halides [Mandar S. Risbud et al], triethylamine hydrochloride [Suneesh P.V. et al].
In the early years of the 20-th century, a new ionic liquids based on mixtures of quaternary ammonium salt-(2-hydroxy-ethyl-trimethyl ammonium chloride) with a number of substances such as hydrogen bonding amide, glycol or acid carboxylic acid (mono-diacid) - to form a solvent capable of dissolving the metal salt and oxide, low cost and ease of recycled or biodegradable without causing pollution.

This new ionic liquids are called DES (deep eutectic solvent). The first publication of this ionic liquid system is of Abbott et al from 2001 to present. In some applications of DES, for electroplating applications are particularly interested in research, which plated silver, copper, zinc, nickel, chromium... as well as their mixtures have been published in the past 5 years. The results of this study showed that ionic liquids DES system is not affected by air and humidity should stabilize in the electroplating process. In addition, the use of DES does not need to add the strong inorganic acids as the other ionic liquid system - factors affecting the environment. It can be seen that the potential of the use of DES in the metal electrodeposition are positive and some areas have been able to the industry. However, the use of DES for aluminum electrodepositing almost many unresolved issues, the number of related works have not been published, whether or not the works mentioned in the present.

The preliminary results of the study we aim to use DES for aluminum plating on the surface of various materials shown appearance aluminum layer structure similar to the structure of the aluminum anode.

2. Experimental Methodology

All the experimental works of this research were carried out in a natural environment of the laboratory except the electrodeposition process is performed in nitrogen atmosphere.

2.1 Chemicals

Choline chloride (p >99%), urea (99.9%), anhydrous aluminum chloride (99.99%), were purchased from Merck (Germany). All used chemicals are of high purity (> 99 %) which must be handled with care.

2.2 Synthesis and Characterization of DESs

The eutectic solvents formed by following the method previously described in many publications [15-30]. In this study, choline chloride and urea are mixed in a glass flask according to the molar ratio, respectively, 1: 1; 1: 2 and 2: 1. The flask was mounted with a magnetic stirrer and heated by oil bath. Nitrogen is added to the flask to remove water vapor and air. Determine the temperature and the time is completely dissolved and the flask put out oil bath, retain nitrogen environment for at least 1 hour. Then, the mixture was dried overnight at 100 °C in a vacuum oven to obtain the final product and prior to the next experiment.

2.3 Measurement of Solubility’s and Physicochemical Properties of Electrolytes of AlCl3 in DES

Measurement of the solubility of AlCl3 in the DES solution was performed by stirring 5% (each 0.015 mol) of AlCl3 in 40 g of DES (each 0.2 mol) and gradually increase the temperature until dissolved AlCl3 in DES. Let cool at room temperature and measuring the physical properties of electrolyst. Same as above with AlCl3 concentration of 10%, 15% and 20% (corresponding to 0.03 mol, 0.045 mol and 0.06 mol AlCl3)

2.4 Study on Cyclic Voltammetry of Electrolyte

In the determination of cyclic voltammograms were performed using an electrochemical workstation Potential - Galvan stat ((PGS-10- Institute of chemistry of Vietnam academy of science and technology-VAST). Platinum working electrode and platinum plate counter electrode were used. A non-aqueous Ag+/Ag electrode, containing the 0.1 mol.L⁻¹ solution of AgNO3 in KCl was employed as reference electrode (RE). As for the electrodeposition experiments, the working, counter and reference electrodes were iron, copper foil, and glassy carbon plate, respectively. Cyclic voltammograms are investigated with Choline Chloride - urea 1:1, and choline chloride / urea / AlCl3 at a temperature of 30°C, amperage of 50 mV/s.

2.5 Electrodeposition of Aluminum on Cathode

The electrodeposition experiments of aluminum on the surface of foil copper, iron foil and plate GC was conducted by galvannostatic method. Electrolyte (cholinechloride / urea / AlCl3) is heated by oil bath at a temperature of 80 - 95°C, the electrical current is 80 - 95 mA and time was 2 h. After electroplating, the cathode was washed with acetonitrile, deionized water and finally dried and determined the weight. Aluminum layer deposited on the cathode was analyzed and determined by methods such as XRD, EDS, SEM.
3. Results and Discussion

3.1 Synthesis and Characterization of DESs

3.1.1 Soluble Choline Chloride and Urea

- Soluble Choline Chloride and Urea at the rate of 1:1 in mole ratio is at 60 °C temperature, dissolved time of 5 minutes. The mixture was transparent and did not crystalized when cooled to room temperature.

- Soluble Choline Chloride and Urea at the rate of 2:1 in mole ratio is at 60 °C temperature, dissolved time of 5 minutes. The mixture was transparent and did not crystalized when cooled to room temperature.

- Soluble Choline Chloride and Urea at the rate of 1:2 in mole ratio is at a temperature of 75 °C, time is 8 minutes completely dissolved. The mixture was transparent, and crystallized fastly when the temperature starts to decrease (less than 75 °C temperature).

<table>
<thead>
<tr>
<th>Choline/urea (mol/mol)</th>
<th>pH</th>
<th>Density (g/ml)</th>
<th>Viscosity (cP)</th>
<th>Electrical conductivity (mS)</th>
<th>Water content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>6.65</td>
<td>1.197</td>
<td>61.5</td>
<td>1.64</td>
<td>650</td>
</tr>
<tr>
<td>2:1</td>
<td>5.92</td>
<td>1.167</td>
<td>57.3</td>
<td>2.96</td>
<td>810</td>
</tr>
<tr>
<td>1:2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1. Physical properties of the solution depends on the rate of choline chloride / urea

Through the survey results of physical properties of the solution depends on the rate of choline chloride as table 1, we chose the DES solution with a choline chloride / urea is 1:1 to carry out research steps next.

3.1.2 Characterization of DES (1:1)

$^1$H NMR (CDCl$_3$, 500 MHz): 3.2(1H), 3.3(5H), 3.5(5H), 4.0(7H), 4.8(1H), 5.7(1H). $^{13}$C NMR (CDCl$_3$, 125MHz): 48.1; 49.5; 67.0; 69.0; 163.5. IR: 3325 cm$^{-1}$ (OH); 3194 cm$^{-1}$ (CH alkyl); 2987 cm$^{-1}$ (CH alkyl); 1607 cm$^{-1}$ (C-C, C-N); 1438 cm$^{-1}$ (CH alkyl deform); 629 cm$^{-1}$ (C- Cl stretch); pH (6.65); Density(1.1971 (g/ml); Viscosity 61.5 (c P); Electrical conductivity(1.64 mS$^{-1}$); Water content (0.065% ~ 650 p.p.m)

3.2 Measurement of Solubility's and Physicochemical Properties of AlCl$_3$ in DES

3.2.1 Solubility

AlCl$_3$ (99.99%) was dissolved slowly in Choline Chloride/Urea with stirring at room temperature in a glove box under nitrogen atmosphere and heated to complete dissolution. Figure 1(a, b, c) are pictures sowed solution after dissolving AlCl$_3$ in DES (1:1) 24 hours and let cool at room temperature.

**Choline chloride 1:1 + 5% AlCl$_3$ solution:**

after dissolving milky-colored liquid, allow to cool at room temperature after 24 hours with no salt crystallization, the solution remains opaque white (Figure 1 a).

**Choline chloride 1:1 + 10% AlCl$_3$ solution**

after dissolving milky-colored liquid, allow to cool at room temperature after 24 hours with no salt crystallization, the solution remains opaque white (Figure 1b).

**Choline chloride 1:1 + 10% AlCl$_3$ solution**

Salt AlCl$_3$ start fading into Cho-urea solution (1:1) at temperatures up to 120°C still not completely dissolved salt, heated to 140°C continue to remain undissolved salt added. Let cool at room temperature after 24 hours, the mixture separated layers (Figure 1c).
3.2.2 Physicochemical properties of electrolytes (DES (1:1) + AlCl₃)

Table 2. Physical properties of liquid choline chloride / urea (1:1) depends on the concentration of AlCl₃ at 30 °C

<table>
<thead>
<tr>
<th>Choline/urea (1:1) + x% AlCl₃</th>
<th>pH</th>
<th>Density (g/ml)</th>
<th>Viscosity (cP)</th>
<th>Electrical conductivity (mS)</th>
<th>Water content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 % AlCl₃</td>
<td>4.30</td>
<td>1.2286</td>
<td>109.1</td>
<td>1.56</td>
<td>950</td>
</tr>
<tr>
<td>10 % AlCl₃</td>
<td>3.18</td>
<td>1.2647</td>
<td>473.1</td>
<td>1.17</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>15 % AlCl₃</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Through the survey results of physical properties of the solution depends on the ratio of AlCl₃ as in table. We chose DES + 5% AlCl₃ solution to carry out the next research steps.

3.3 Study on Electrochemical of DES (1:1) and DES (1:1) +5% AlCl₃

In Figure 2, Cycle Voltammograms on the working electrode (WE) of the electrolyte without the presence AlCl₃ differ quite clear:

For GC working electrode is an increase in the slope-to-3 V 4 V, 2 V and stability to. Then there is a steep increase at 4.5 V and 7 V descending to the ring back and closed at 1.5 V to -1 V. Limit in cathode located from -2V and in the anode is limited at +2 V, resulting ECW is 4 V.

For the copper working electrode, the cathode is limited to -1.4 V and -0.6 V is anode limited. Since it is only 0.8 V ECW. Meanwhile, the WE cathode is limited only Iron -1 V and anode is limited to -0.2 V, resulting in only a 0.8 V ECW (Table 2).
Table 3. ECW of solution Choline Chloride - Urea (Molar ratio 1:1)

<table>
<thead>
<tr>
<th>Working cathode (WE)</th>
<th>Cathode limit</th>
<th>Anodic limit</th>
<th>ECW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glassy Carbon</td>
<td>-2V</td>
<td>2V</td>
<td>4V</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>-1.4V</td>
<td>-0.6V</td>
<td>0.8V</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>-1V</td>
<td>-0.2V</td>
<td>0.8V</td>
</tr>
</tbody>
</table>

When the presence of AlCl₃, Cycle voltammograms picture on the working electrode (WE) of electrolyte changes considerably better for GC, worse for copper and iron (figure 3).

While limits of GC cathode pulled down to -3.5 V, the limit of copper cathode and iron only - 0.43 V and - 0.875 V, respectively. On the other side, the anode limit of the GC reduced at 2 V compared with 1.5 V and of Iron from - 0.2 V to - 0.625 V, respectively. Meanwhile, copper for WE is occurring phenomenon increased from -0.6 V to - 0.42 V. The results of electrolyte ECW on making the presence of 5% AlCl₃ increased from 4 V to 5 V for the GC, was reduced from 0.8 V to 0.1 V for copper and from 0.8 V to 0.1 V for iron (Table 4).

Table 4. ECW of solution Choline Chloride - Urea (Molar ratio 1:1) with 5% AlCl₃

<table>
<thead>
<tr>
<th>Working cathode (WE)</th>
<th>Cathode limit</th>
<th>Anodic limit</th>
<th>ECW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glassy Carbon</td>
<td>-3.5V</td>
<td>1.5V</td>
<td>5V</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>-0.43V</td>
<td>-0.42V</td>
<td>0.1V</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>-0.875V</td>
<td>-0.625V</td>
<td>0.3V</td>
</tr>
</tbody>
</table>

The results showed that, for choline chloride electrolyte/urea 1:1 + 5% AlCl₃ can be used for electro-deposition of alumina on the aforementioned electrodes with very little amperage. This is consistent with some previous studies for other ionic liquids. Osteryoung and Welch proved that the aluminum deposition process can be reversed (in an ionic liquid butylpyridinium chloride/AlCl₃) [31]. Deposition occurred at -0.43 V and oxidation was observed at -0.22 V. Lay and Skyllas-Kazacos [32] studied the electrodeposition of aluminum on GC electrode in liquid imidazolium with tetrachloroaluminate at -0.2 V. The same phenomenon also on the iron electrode was observed at 0.2 V.

3.4 Electrodeposition of Aluminum on Cathode

Aluminum electro-deposition process was carried out in equipment as described in section 2.5. Some technical indicators of the experiment are shown in Table 5 below.

Table 5. The data of electro-deposition aluminum process on the different electrodes

<table>
<thead>
<tr>
<th>STT</th>
<th>Cathode</th>
<th>Voltage (V)</th>
<th>Temperature (°C)</th>
<th>Area electrodes (cm²)</th>
<th>The distance between the cathode and anode (cm)</th>
<th>Current (mA)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>GC</td>
<td>-2</td>
<td>80-95</td>
<td>3</td>
<td>2.5</td>
<td>80-95</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>Cu</td>
<td>-1.5</td>
<td>80-95</td>
<td>3</td>
<td>2.5</td>
<td>80-95</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>Fe</td>
<td>-1</td>
<td>80-95</td>
<td>3</td>
<td>2.5</td>
<td>80-95</td>
<td>2</td>
</tr>
</tbody>
</table>

The previous study showed that the electro-deposition of Al can only be done in an electrolyte solution is acidic, which causes ion Al₃Cl₇⁻-reduction arising aluminum (Al⁺³) to convert the aluminum surface cathode side, after receiving 3 electrons:

\[ 4\text{Al}_3\text{Cl}_7^- + 3\text{e}^- \rightarrow \text{Al} + 7\text{AlCl}_4^- \]

Also, aluminum oxide can form on the surface of the cathode, where the presence of oxygen or water. This suspicion can be removed because of the water content in the electrolyte solution our very low (Table 2) and nitrogen gas was bubbled directly into the solution during electroplating. The EDS analysis results can indicate the following things.
Based on the weight change of the anode (aluminum) conducted before and after electrodeposition, may determine the amount of aluminum is lost from the anode. Similarly can determine the weight of aluminum deposited on the cathode surface. The experimental results are shown in Table 6 and digital picture of the cathode is shown in Figure 7.

Table 6. Results aluminum electro-deposition on the cathode

<table>
<thead>
<tr>
<th>Anode and Cathode</th>
<th>Experiment 1</th>
<th>Experiment 2</th>
<th>Experiment 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al-anode</td>
<td>GC-cathode</td>
<td>Al-Anode</td>
</tr>
<tr>
<td>The weight after EP</td>
<td>5.7610</td>
<td>4.4032</td>
<td>5.6332</td>
</tr>
<tr>
<td>Weight differences</td>
<td>0.3412</td>
<td>0.1052</td>
<td>0.3680</td>
</tr>
<tr>
<td>% Al-coated on cathode</td>
<td>30.83</td>
<td>64.45</td>
<td></td>
</tr>
</tbody>
</table>

Results in Table 6 show that the mass loss of aluminum from the anode approximately equal for all three experiments and accounted for about 5.6 to 6% by weight of anodes. Meanwhile, the amount of aluminum coated on the cathode there is a difference: for iron cathode, aluminum coated over 60%, while for the GC and copper cathode, aluminum coated only at 30%. While that digital camera pictures of surface cathodes in Figure 7 shows the surface of copper and GC cathodes are smooth and finely than the iron cathode surface.

![Digital pictures of cathodes plated.](image)

One of the reasons for the deposited aluminum layer is not glossy and smooth, can be deposited by aluminum impurities. This result was verified by EDS analysis following.

3.5 Analysis and Characterization of Aluminum Coatings

3.5.1 Energy Dispersive X-ray Analytics (EDS)

The analytical results Energy dispersive X-ray Analytics (EDS) component of aluminum coated on the surface of the cathode is made on equipment JEOL JED 2300 in accordance with analytical methods on the device Spectro's XRF analyzers from AMETEK Materials Analysis Division. On the figure 5, 6 and 7 are EDS spectrum of the aluminum layer is coated on the cathode.
Table 7. Component elements exist in aluminum deposited layers on three cathode

<table>
<thead>
<tr>
<th>Element</th>
<th>GC</th>
<th>Fe</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass-%</td>
<td>Mass-%</td>
<td>Mass-%</td>
</tr>
<tr>
<td>Al</td>
<td>92.42</td>
<td>70.33</td>
<td>82.63</td>
</tr>
<tr>
<td>Cl</td>
<td>7.58</td>
<td>9.45</td>
<td>10.63</td>
</tr>
<tr>
<td>Fe</td>
<td>-</td>
<td>7.19</td>
<td>-</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>13.03</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>-</td>
<td>-</td>
<td>6.74</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

The spectrum showed the highest peak of aluminum and clear. On the cathode surface is GC, because no other metals to purity of the aluminum coating can reach 92%. For iron and copper cathode, these metals covered a part of aluminum layer, should result is decreased purity of aluminum. In addition, we also found a number of
chlorine are present on all three cathode, it is possible contamination of AlCl$_3$ on the cathode surface. The presence of sulfur on the cathode made of iron, iron sulfate can be formed in stages cathode surface cleaning with dilute sulfuric acid solution. Sum up results of identified elements exist on the aluminum cathode layer are shown in Table 7.

3.5.2 X-ray Diffraction (XRD)

XRD patterns of aluminum deposits were collected on X-ray diffractometer Bruker D8 Advance and the acquired diffraction pattern of the obtained sample shows only the pattern of aluminum metal (Figure 8). The diffraction peaks attributed to pure Al with a face-centered cubic structure (fcc) were clearly detected from the sample of electrodeposited aluminum layer on Cu cathode. Similar results were observed for other samples of aluminum on GC and Fe cathode.

![Figure 8. XRD pattern of the Al anode and Aluminum electrodeposit on copper cathode](image)

3.5.3 Scanning Electron Microscope (SEM)

SEM was measured on Ultra-high Resolution Scanning Electron Microscope S-4800 (HITACHI). In Figure 9a is SEM image of cathode copper, taken at 20 micron. Although it has been carefully cleaned but still see the lines on the surface. In Figure 9b is the SEM image of copper cathode taken at 300 nm. Figure 9c shows the aluminum anode surface taken at 300nm. There the similarity of the surface entirely made of aluminum cathode (9b) with aluminum layer deposited on a copper cathode (9e-300nm). Figure 9d show aluminum layer deposited on the copper cathode, taken at 20 micron.
Figure 9. SEM images of copper cathodes surfaces (a) and aluminum layer on cathode (b)

4. Conclusions
From the experimental results mentioned above, one can draw the following conclusions:

1) Electrolyte system can use chloride choline / urea (1:1) with 5% AlCl₃ to perform electrodeposition on aluminum cathode copper, iron and GC at temperatures between 80-95 °C with voltage from -1 to -2 depending on the cathode material and amperage stable at 80-95 mA in 2 hours.

2) The amount of aluminum transferred from the anode to the cathode depends on the cathode material, and achieved 30.8% for GC; 64.45% for Fe and 29% for copper. Purity of aluminum on the cathode varied from 92.42% for GC, 70.33% for Fe and 82.63% for Copper. Need for further research to improve the purity of the aluminum on the cathode.

Acknowledgements
The authors gratefully acknowledge the financial support of the Vietnam Academy of science and technology through Research Program of Materials Science VAST 03.07/13-14

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