TOWARDS AN ELECTROLESS DEPOSITION OF GOLD ON METALLIC SUBSTRATES USING IONIC LIQUIDS AS ELECTROLYTES

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ABSTRACT: Recent research has suggested a number of applications for gold in fuel cells and related hydrogen fuel processing, which include coatings for light weight corrosion resistance bipolar plates and the incorporation of gold as catalyst to provide improvements in electrode conductivity, among others. This paper reports on the electroless deposition of gold on copper substrates from a HAuCl₄·3H₂O solution in 1-butyl-1-methylpyrrolidinium dicyanamide (BMP-DCA), in normal atmospheric conditions. The electrochemical behaviour of the plating solution was studied by potential sweep techniques. Results indicate that gold ions are deposited on copper without the aid of external polarization. The deposition process probably involves a displacement reaction involving copper dissolution, since no other oxidation reaction was identified. Preliminary studies using SEM/EDX showed that gold thin films, deposited on copper substrates at 333 K, present a granular nanostructured morphology, typical of electrodeposited films from DCA containing ionic liquids.

Keywords: Electroless deposition, Gold, Ionic Liquids, Thin films.

1. INTRODUCTION

There is an increasing interest in gold deposition for fuel cells applications, associated to the high corrosion/passivation resistance conferred to less noble substrates and to its catalytic properties. In the first case, gold coatings are being used in Polymer Electrolyte Membrane (PEM) bipolar plates to improve the performance of the materials currently tested, such as titanium or stainless steel [1, 2]. As a catalytic material, gold can have a significant role in the purification of hydrogen to be supplied to fuel cells as well as in the design of new catalysts [3].

Gold coatings are generally produced by electrodeposition using bath formulations that contain cyanides [4] and other toxic additives. Ionic liquids provide an alternative path with reduced health and environmental impacts due to the low
volatility, while maintaining suitable properties to be used as electrolytes. In fact, ionic liquids have high chemical and thermal stability, and a conductivity which is, at least, equivalent to other organic solvents with added supporting electrolyte [5]. Under inert and dry conditions, the electrochemical window of some ionic liquids can extended up to 6 V, allowing the electrodeposition of metals outside the potential range for the chemical stability of water, such as aluminium or tantalum [6, 7]. Recently, ionic liquids (Figure 1) have been examined as new electrolytes for electroplating different single metals (including gold), alloys or semiconductors materials [8]. The reduction of gold ions in ionic liquids has been mainly examined by voltammetry. Xu and Hussey were the first to report the reduction of gold ions from a solution of AuCl₄⁻ in an aluminium chloride-1-ethyl-3-methylimidazolium chloride mixture, working in dry and inert atmospheric conditions [9]. They found two sequential reduction peaks on the voltammogram performed, associated with the reduction of [AuCl₄]⁻ to [AuCl₂]⁻ and [AuCl₂]⁻ to Au⁰ respectively [9]. Other authors have also found a two-step reduction after the addition of Au⁺ to different imidazolium ionic liquids, including 1-butyl-3-methylimidazolium bis(trifluoromethyl)sulfonyl imide (BMI-TFSI) [10, 11] and 1-ethyl-3-methylimidazolium tetrafluoroborate (BMI-BF₄⁻) [12] on gold, platinum or glassy carbon electrodes. However, it has also been found that reduction of gold occurs by a single step, from Au⁺ to Au⁰, after the initial deposition of gold from the liquid BMI-BF₄⁻ on a glassy carbon electrode [12].

![Chemical formulae of common ionic liquids, based on imidazolium and pyrrolidinium cations, used for electrodeposition.](image)

**Figure 1.**

The possibility of depositing gold thin films in an electroless fashion, presents some advantages when compared with electroplated gold: no external power or elaborate equipment is necessary to produce thin uniform coatings, and it is more suitable to coat surfaces which include groves or other particular shapes such as PEM fuel cell bipolar plates.

Although the term electroless is usually referred to all the deposition processes that may occur without an external source of polarization, it is more correctly used, when the process, occurring at the open-circuit, is autocatalytic. In this case, the reduction of metal ions, dissolved in the electrolyte, is balanced by the oxidation of species from the solution. The deposits obtained in this way may grow relatively thick, since there is no limitation imposed by reaction from the substrate. The deposits can also be formed on non-conductive substrates because there is no direct involvement of the substrate in the redox reactions. Deposits may also be formed at the open-circuit by a different mechanism known as displacement deposition. It occurs as a consequence of the reduction of metal ions dissolved in the electrolyte and the oxidation of the substrate, which is less noble than the metal to be reduced. This process produces relatively thin films since the process stops after the substrate is covered by the noble metal. Usually, the obtained deposits are porous due the anodic reaction that occurs from the substrate itself [13].

Results of electroless gold deposition from ionic liquids are scarce. Alldous et al [10] found that a thin film of gold was obtained on a glassy electrode from a solution of 0.05 M HAuCl₄ dissolved in BMI-TFSI. The deposits show an irregular multifaceted growth which includes triangular and hexagonal forms with sizes between 0.1 and 1 µm. It was necessary a period of time of 18 h to obtain an eye-visible layer. The deposition mechanism is unclear, but is probably associated with the reductive sorption of the gold species at active sites on the carbon surface [10]; the authors also found that deposition is prevented if a different anion is used, like PF₆⁻ or BF₄⁻, or if water is added to the solution. Qin et al [14] also produced thin deposits of gold without any external polarization. The deposits were nanocrystalline with a dendritic structure and were obtained on zinc substrates from a 0.015 M HAuCl₄ + BMI-PB₆ solution as the electrolyte. The zinc substrates were immersed in the ionic solution and placed in an oven at 60°C for 4.5 h, without any drying procedure. The first gold crystals were formed on the substrate by the displacement mechanism. Crystal growth took place preferentially on the previously formed crystals sites, from which hyperbranched dendrites were firstly developed. This is a very interesting feature, since the same authors also found that a zinc substrate immersed in an aqueous solution of 0.015 M HAuCl₄ of pH 1.98, submitted to the same deposition conditions, develops an irregular nanocrystalline alloyed deposit of Au-Zn [14].

In this work, 1-butyl-1-methylpyrrolidinium dicyanamide (BMP-DCA) ionic liquid is selected as a possible electrolyte for electroless gold deposition. The selection was based on the physical and chemical properties of the ionic liquid, including the viscosity, conductivity and complexing ability [15]. Moreover, using ionic liquids based on the pyrrolidinium cation a nanocrystalline structure of the deposited metal is expected [16-18], without the need for other additives. The experiments were conducted in an open cell in laboratory atmospheric conditions. Preliminary characterization of the gold coating deposited on copper substrates was done by surface SEM observation and EDX analysis. In order to better understand the deposition process, voltammetry was performed on glassy carbon and copper electrodes.

### 2. Experimental Procedure

The electrolyte for gold plating was prepared from analytical grade chemicals in the as-received condition, by dissolving HAuCl₄·3H₂O (ACROS) in 1-butyl-1-methylpyrrolidinium dicyanamide (BMP-DCA) to a concentration of 0.020 M. The ionic liquid used was from Merck with a purity > 98%, containing less than 1% of H₂O and ≤ 0.1% of halides. The
electrochemical experiments were performed using a 10 mL electrochemical cell with a three electrode configuration, exposed to laboratory atmosphere. The potential was measured against a platinum wire, considered a quasi-reference electrode (QRE). The counter electrode was a platinum foil (area ~ 1 cm²). Before the electrochemical experiments, the platinum electrode was activated by dipping in HNO₃ (65%) during one minute. Copper electrodes of commercial purity were polished, firstly with carbon paper (1000 mesh) and then with diamond paste of 6 and 3 µm. Finally the specimens were activated by dipping in a H₂SO₄ solution (1:10). The electrochemical data were acquired with a potentiostat (EG&G PAR, model 173) using “Corrware” software. A Philips Scanning Electron Microscope, Model XL 30 FEG, equipped with energy dispersive X-ray spectroscopy (EDX) was used.

3. RESULTS AND DISCUSSION

3.1. Solvent selection

The solvent chosen for deposition was 1-butyl-1-methyl-pyrrolidinium dicyanamide (BMP-DCA). Table 1 compares physical properties such as conductivity, viscosity and density at room temperature, for some ionic liquids or mixtures already used in gold deposition studies [19,5,20]. The BMP-DCA seems to be the best choice since it presents the most favorable values of viscosity and conductivity required for an efficient mass transfer. It has also the advantage of not having fluoride ions in its constitution, which usually originates hydrofluoric acid if water is present. There are two other characteristics that strengthen the choice of BMP-DCA: firstly, it has a strong complexing ability, based on the Lewis character of the DCA anion, which promotes high solubility of many metal chlorides [15] and second, it has been suggested that ionic liquids based on the pyrrolidinium ion induces a nanocrystalline structure on metal deposits, without the need for additives, as already stated in the introduction [16-18]. One of the drawbacks is that BMP-DCA is very hygroscopic. In this particular case, it is seen as an advantage, since the uptake of water by the ionic liquid contributes to increase the conductivity of the electrolyte without hindering gold deposition. In view of the mentioned properties, BMP-DCA was selected, in this work, as potential solvent for the deposition of gold without the aid of external polarization.

Table 1 Physical properties of the ionic liquids and mixtures already used for gold electrodeposition.

<table>
<thead>
<tr>
<th>IonicLiquid/ Physical property</th>
<th>BMI-Cl + AICl₅ (50%)</th>
<th>BMI-BF₄</th>
<th>BMI-PF₆</th>
<th>BMP-DCA</th>
</tr>
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* in this work (without any drying procedure and exposed to normal atmospheric conditions).

3.2. Gold deposition and film morphology

Thin films of gold were obtained, in laboratory atmospheric conditions, by exposure of copper substrates to a solution of 0.020 M HAuCl₄·3H₂O in BMP-DCA, at 333 K, during 1500 s and without any external polarization. After immersion, the registered open-circuit potential (Eoc) was initially -0.900 V. A slight decay to -0.910 V occurred during the first 35 s of exposure time; after that, an increase up to a plateau at -0.863 V was observed (Figure 2), followed by a new progressive increase in potential up to a maximum at -0.840 V after which the potential decreased to -0.854 V. At the end of the experiment and after a rinse with water and drying in cool-air, it was visible that the electrode was covered with a golden brown film.

SEM observations of the obtained film are presented in figure 3. EDS analysis confirms the presence of gold and copper (Figure 3b): no other elements such as oxygen, chlorine or nitrogen were detected. The film seems to cover the entire substrate surface (Figure 3a), but SEM observations at higher magnification showed some porosity in the deposited layer (Figures 3c and 3d). The film show a granular morphology and it is constituted by aggregates of nanoparticles (Figure 3d), which seem to have grown in size until they are limited by the close contact with other aggregates that are growing on the surrounding area. This effect promotes a coarse distribution on the aggregate size, with a diameter in the range of 50 nm to 300 nm (Figure 3d). It was possible also to observe a few cracks on the deposited layer which is associated to the film internal stress.

3.3. Electrochemical behavior of copper in BMP-DCA

In order to better understand the open-circuit deposition of gold on copper in BMP-DCA, a preliminary study on the electrochemical behavior of the system Cu/ BMP-DCA was carried out.

A polarization curve was run in BMP-DCA using a copper substrate as a working electrode. The potential was scanned within the range from -1.5 to +0.5 V vs Pt (QRE) at a potential sweep rate of 100 mV s⁻¹. Results obtained in laboratory
No peaks directly associated to the reduction of gold ions were identified on the voltammograms obtained for copper.

However, voltammograms obtained in the same experimental conditions for a glassy carbon electrode at 298 and 333 K (Figure 5) show two cathodic peaks identified as C\textsubscript{I} and C\textsubscript{II} respectively. At 298 K, the peak C\textsubscript{I} and C\textsubscript{II} are located at potentials of -0.630 V and -1.193 V respectively. Equivalent peaks were obtained at 333 K, but slightly displaced to less negative potential, as expected due to temperature activation of the processes. The peaks are probably associated to the reduction of gold species: from Au\textsuperscript{3+} to Au\textsuperscript{+} and Au\textsuperscript{+} to Au\textsuperscript{0}, as it has been reported for gold deposition from other ionic liquids [9-12]. So far, it is difficult to specify the chemical species involved on the reduction of gold because both ions, anion and cation, can have a significant influence on the redox and interface processes involved. The dicyanamide ion is well-known due to the strong ability to form complexes, so it is possible that gold dicyanamide complex species are formed by replacing the chlorides from the ion AuCl\textsubscript{4}\textsuperscript{-}. For example, a study on nickel deposition from a solution of NiCl\textsubscript{2} in EMI-DCA suggests that it is the complex species Ni[DCA]\textsubscript{4} which is reduced to Ni\textsuperscript{0} [22]. The presence of water can not be disregarded because, at least in aqueous solutions of AuCl\textsubscript{4}\textsuperscript{-}, there is a replacement of chloride by hydroxyl groups up to four (depending on pH) [23]. Finally, the pyrrolidinium ion, which has been used to prepare gold nanoparticles by thermal reduction [24], can also interfere due to the strong absorption on the metal surface [25] and consequently interfere with reactions which have to occur for gold reduction.
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Fig. 5. Cyclic voltammograms obtained for glassy carbon in pure BMP-DCA and BMP-DCA + 0.020 M HauCl₄.3H₂O solution at 298 K and 333 K.

The polarization curves carried out in pure BMP-DCA and BMP-DCA + 0.020 M HauCl₄.3H₂O solution show that copper is easily dissolved in both solutions since there is a significant increase of the current density above the open-circuit potential. So, it seems that the complementary oxidation for the reduction of gold ions will be the copper oxidation, when the system is left at the open-circuit.

The results show that gold films can be obtained on copper substrates from a solution of 0.020 M HauCl₄.3H₂O in BMP-DCA at the reported experimental conditions. The potential of open-circuit, -0.900 V, is not very far from the potential of the reduction of Au⁺ to Au⁰, which suggest that the displacement of copper by gold is the most probable process. SEM observations at high magnification show that the films are formed by only one layer of aggregates which do not cover completely the surface. Since copper takes an active part in the deposition process, it is necessary to have some copper surface in direct contact with the solution, otherwise the process stops. This feature is a characteristic of this process, and some porosity is always expected associated to this type of deposition.

4. CONCLUSIONS

This work evidences that thin films of gold are obtainable on copper under laboratory atmospheric condition and without the aid of any external polarization source in a solution of 0.020 M HauCl₄.3H₂O in BMP-DCA.

The gold films deposited on copper substrates at 333 K for 1500 s, consist of nanoparticles aggregates with a coarse distribution in size, with a diameter less than 300 nm. The film show some porosity which might be related to the deposition process: the displacement of copper by gold.

Further investigation is necessary to further characterize the film and to find the most favorable experimental conditions to obtain more uniform and compact films.


