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# Gold deposition from 1-butyl-1-methyl-pyrrolidinium dicyanamide ionic liquid at open-circuit and under potentiostatic control

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## ABSTRACT

In this work, the deposition of gold on copper substrates from solutions of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  in 1-butyl-1-methylpyrrolidinium dicyanamide was studied. Deposition was carried out in open-circuit and under potentiostatic control at temperatures from 293 to 353 K, in normal atmosphere, with deposition conditions allowing water from atmospheric absorption up to 0.8 wt.%. Films of gold were obtained by both methods. Deposition at open-circuit occurs by galvanic displacement mechanism. Involvement of  $\text{Cu}^+$  species in the electrodeposition process was suggested by cyclic voltammetry. Furthermore, copper incorporation in the gold films was confirmed by X-ray diffraction. SEM observation and XRD analysis show that films are nanocrystalline with a globular morphology except for the films formed under potentiostatic control at 353 K, which show a dendritic structure. The size of the crystallites determined by Scherrer's equation varies in the range from 6 to 25 nm.

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## 1. Introduction

Gold nanostructured films are well-known for their electrocatalytic properties [1,2] and a promising route to obtain them is through the electrodeposition from gold salt solutions in ionic liquids (ILs). The high chemical activity of their surfaces is directly related to the metastable state of surface atoms [2,3], which depends on size and shape of the catalytic nanoparticles. Recently, it has also been shown that different faces of gold faceted crystals have different reactivity for specific reactions [4], which means that gold surfaces can be tailored to increase the yield of a particular reaction. However gold nanocrystalline catalysts require some type of support to achieve mechanical strength, for example by depositing them on a metal substrate. In the present work, copper was used as substrate for gold deposition due to its high electrical conductivity and chemical stability.

Ionic liquids present a large electrochemical window, high chemical and thermal stabilities and low environmental and health impacts. They have been tested as an alternative to aqueous electrolytes for the electrodeposition of a wide range of materials, including reactive metals and alloys [5–10]. For example, thin films of aluminum [9] and tantalum [10] could be produced because there are no longer restrictions imposed by metal oxidation or hydrogen evolution, contrarily to what occurs with aqueous solutions. Furthermore, ionic liquids favor the formation of nanocrystalline films and nanostructured surfaces [11–15]. The deposition of gold from solutions of auric chloride in several ionic liquids has been

previously reported [16–19]. These studies showed that the deposition of gold is a two-step process, the first corresponding to the reduction of the complex ion  $[\text{AuCl}_4]^-$  to  $[\text{AuCl}_2]^-$  and the second one to the reduction of  $[\text{AuCl}_2]^-$  to  $\text{Au}^0$ . A two-step reduction mechanism, from  $\text{Au}^{3+}$  to  $\text{Au}^+$  and from  $\text{Au}^+$  to  $\text{Au}^0$ , was also observed by the present authors for the deposition of gold from a 0.020 M solution of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  in 1-butyl-1-methylpyrrolidinium dicyanamide (BMP-DCA) on nickel and glassy carbon in normal atmosphere conditions [20]. In that work, continuous films of nanocrystalline gold were obtained on nickel substrates under potentiostatic control at  $-1$  V. The deposits present a globular morphology when deposition was carried out at 333 K and a dendritic morphology at 353 K. More recently, Monzon et al. [21] compared the morphology of gold deposits obtained by the reduction of auric complex ions in different aqueous and organic solvents, including the ionic liquid 1-butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl) imide (BMI-TFSI), and concluded that organic solvents have a strong influence on the shape and size of the deposited particles because these solvents are absorbed at the film surface, limiting the crystal growing.

The electroless deposition of gold from ionic liquid solutions was also reported by several authors. Aldous et al. [18] observed the deposition of gold on glassy carbon in open-circuit conditions from a solution of  $\text{HAuCl}_4$  in BMI-TFSI. The deposition rate was extremely low, an immersion period of 24 h being required to visualize the deposited gold and even after this long period of time, the deposit consisted of scattered aggregates of gold nanoparticles. The authors also refer that deposition is hindered by the presence of water in the electrolyte, the use of  $\text{NaAuCl}_4$  as gold donor or when the anion of the ionic liquid was changed to  $\text{PF}_6^-$  or  $\text{BF}_4^-$  [18]. Dendritic deposits of gold were observed on zinc substrates, prepared by electroless

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