Journal of Electroanalytical Chemistry 657 (2011) 54–60

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Gold electrodeposition in organic media

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ARTICLE INFO

Article history:
Received 7 December 2010
Received in revised form 7 March 2011
Accepted 10 March 2011
Available online 17 March 2011

Keywords:
Tetrabutylammonium
Shape-control agent
SEM
AFM
Voltammetry
Kinetic constant

ABSTRACT

Organic species are easily adsorbed onto metal electrodes, due to the high surface energy. This principle is widely employed in electrodeposition to obtain grains with a given shape and size. Electrodeposition in organic electrolytes and ionic liquids is expected to produce deposits whose properties will be modified by the nature of the species present in the bath. Here, we analyse the voltammetric profiles for the reduction of two different gold complexes, tetrachloroaurate (III) ($AuCl_4^-$) and dicyanoaurate (I) ($Au(CN)_2^-$), in dimethylsufoxide (DMSO) and in the ionic liquid tributylmethylammonium bis(trifluoromethylsulfonyl)imide ($TBMA^+NTf_2^-$). We evaluate how organic cations present in the electrolyte modify not only the voltammetric response but also the morphology of the deposits obtained. The films range from very smooth with a rms roughness of ~10 nm for 500 nm film to rough globular or facetted films with a crystalline size of ~200 nm.

1. Introduction

The electrodeposition of highly electropositive metals is performed in electrolytic baths, where high voltages are accessible. At present, materials such as Al, La, Ta, Ga, Na and Si, among others, are deposited in organic electrolytes or ionic liquids, where the chemical stability of the organic species leads to a wider potential window [1–6].

Capping agents are used in electrodeposition to guide the growth of metal or semiconductor crystals [7–19]. These organic species adsorb onto electrodes and electrodeposits as a result of the high surface energy of these materials, which ultimately influence the shape of the growing grains. Therefore, the chemical nature of the organic ions present in ionic liquids and organic electrolytes may have a strong impact on the morphology of the deposits produced. To address this, we chose to electrodeposit a noble metal, gold, because the films obtained remain stable after exposure to air, allowing the morphology to be readily characterised.

We analyse the cyclic voltammograms of $AuCl_4^-$ and $Au(CN)_2^-$ in dimethylsulfoxide (DMSO) containing different electrolytes. The adsorption of tetrabutylammonium (TBA^+) onto the electrode surface is evaluated through the electrochemical characterisation of the reduction of $AuCl_4^-$. The voltammetric profiles are correlated with the SEM images of the films. Images of deposits grown in the ionic liquid tributylmethylammonium bis(trifluoromethylsulfonyl)imide ($TBMA^+NTf_2^-$) are included for comparison. Although the electroreduction of $AuCl_4^-$ in organic media has been reported [20–23], the physicochemical aspects of the differences with its reduction in water were not discussed. Here, we analyse the thermodynamic aspects involved during this process and their implications.

2. Experimental

Electrochemical measurements were carried out in a Braun 130 glovebox with O_2 level <1 ppm and H_2O 3–4 ppm using a CHI 660 potentiostat, with iR drop compensation. A three-electrode arrangement was used. A gold disc 5 mm diameter was employed as the working electrode and platinum mesh as the counter electrode. The reference electrode was a commercial silver wire in a capillary tube immersed in the supporting electrolyte solution employed and separated from the analyte solution by a porous frit. After each experiment, a ferrocene solution was added as an internal standard to set the potential scale. The working electrode was polished prior to every experiment with 1 μm, 0.3 μm and 0.05 μm alumina slurries on lapping pads, followed by electrochemical cleaning in a 0.2 M H_2SO_4 solution purged with Argon: potential pulses of 2 s at 2 V and −2 V vs. Ag/AgCl/0.1 M Cl^- were applied during 1 min. The electrode was rinsed with deionised water, carefully dried with N_2 and transported into the glovebox.

Dimethylsulfoxide (DMSO) anhydrous was dried with activated molecular sieves, 4 Å (Sigma). The molecular sieves were activated in a furnace at 350 °C during 1 day and added to the DMSO. The solvent was allowed to dry for 1 week and stored in the glovebox. The supporting electrolytes employed were tetrabutylammonium (TBA^+) or potassium perchlorate (Sigma). They were dried at

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doi:10.1016/j.jelechem.2011.03.010

70 °C under vacuum. Anhydrous potassium tetrachloroaurate (III) and potassium dicyanoaurate (I) were obtained from Sigma and opened, weighted and always kept in a dried atmosphere. $\mathrm{TBMA^+NTf_2^-}$ ionic liquid was prepared via metathesis of tributylmethylammonium chloride and lithium bis(trifluoromethylsulfonyl)imide, in water. Gold salts soluble in the ionic liquid were synthesised in a similar fashion. An aqueous solution of tributylmethylammonium chloride was added to an aqueous solution of potassium tetrachloroaurate (III) or potassium dicyanoaurate (I) to produce ($\mathrm{TBMA^+AuCl_4^-}$) or ($\mathrm{TBMA^+Au(CN)_2^-}$) respectively. $\mathrm{TBMA^+AuCl_4^-}$ precipitate as a yellow solid and ($\mathrm{TBMA^+Au(CN)_2^-}$) separates from the aqueous solution as an oily phase. $\mathrm{TBMA^+AuCl_4^-}$ was purified by recrystallization and dried at 80 °C. $\mathrm{TBMA^+Au(CN)_2^-}$ and $\mathrm{TBMA^+NTf_2^-}$ were washed with water several times and dried under vacuum at 80 °C overnight. For SEM images, the films were grown potentiodynamically, on gold substrates with an exposed area of 1.13 cm^2. The Au/Si(1 0 0) substrates were prepared by e-beam evaporation of 20 nm of chromium followed by 100 nm of gold using a BOC Edwards Auto 500 evaporator (base pressure: 5×10^{-7} mbar). Prior each electrodeposition, they were cleaned with $\mathrm{H_2O_2}$ + 1 M KOH, followed by electrochemical stripping in 1 M KOH [24]. The clean substrates were blown with $\mathrm{N_2}$ and transported into the glovebox. Voltammetric simulations were carried out, employing the windows-based software supplied with the 660 CHI potentiostat.

The surface topography and roughness (rms) of some of the resulting films were also determined using an Asylum MFP-3D atomic force microscope (AFM). Morphology and composition were studied by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX).

3. Results and discussion

3.1. Electrochemistry of $\mathrm{AuCl_4^-}$

In aqueous solutions, the reduction of $\mathrm{AuCl_4^-}$ to metallic gold takes place via a single three-electron process [25–27]. $\mathrm{AuCl_2^-}$ does not appear as an intermediate in aqueous solutions because its formation is less favourable (the standard redox potential for the reduction of $\mathrm{AuCl_4^-}$ to metallic gold is larger than to $\mathrm{AuCl_2^-}$).

$$\mathrm{AuCl}^-_{4(aq)} + 3\mathrm{e}^- \rightarrow \mathrm{Au}_{(s)} + 4\mathrm{Cl}^-_{(aq)} \quad E^0 = 1.002\ \mathrm{V\ vs.}\ NHE \tag{1}$$

$$\mathrm{AuCl}^-_{4(aq)} + 2e^- \rightarrow \mathrm{AuCl}^-_{2(aq)} + 2\mathrm{Cl}^-_{(aq)} \quad E^0 = 0.926\ \mathrm{V\ vs.}\ NHE \tag{2}$$

In organic solvents [20,21] and ionic liquids [22,23], on the other hand, this reduction occurs in two consecutive electrochemical steps, at two different potentials:

$$\mathrm{AuCl}^-_{4(o)} + 2e^- \rightarrow \mathrm{AuCl}^-_{2(o)} + 2Cl^- \quad E_1 \tag{3}$$

$$\mathrm{AuCl}^-_{2(o)} + e^- \rightarrow \mathrm{Au}_{(s)} + 2Cl^- \quad E_2 \tag{4}$$

To the best of our knowledge, no physicochemical explanation has been given for this difference. We think that a possible reason might be the poor solvation of $\mathrm{Cl^-}$ ions in aprotic solvents and ionic liquids. It is accepted that the solubility of small anions is determined by the electron pair acceptability of the solvent, which in the case of DMSO is 19.3 against 54.8 for water [28]. Therefore, the solvation of DMSO towards halide ions is predicted to be much weaker than it is in water, making the release of four $\mathrm{Cl^-}$ in one single step thermodynamically unlikely. In the case of ionic liquids, the solubility of halides is mainly determined by supra-molecular interactions with the cation of the ionic liquid. Given the low dielectric constant of ionic liquids, typically ∼10 [29,30], the ion-pair interactions are strong [31,32]. It has been shown that even small amounts of $\mathrm{Cl^-}$ ions dissolved in ionic liquids increase their viscosity dramatically [33], which reflects the structuring effect exerted by such small hydrophilic ions. This is in agreement with thermodynamic calculations that predict solvation entropies of halides in ionic liquids to be negative [34]. All this evidence indicates that the insertion of $\mathrm{Cl^-}$ in ionic liquids or aprotic solvents modifies the solvent environment unfavourably, increasing the energy barrier of the overall electrochemical reaction. A similar behaviour was reported in the electrochemistry of $\mathrm{TiCl_4}$ in ionic liquids, where the impossibility of electrodepositing Ti was attributed to 'kinetics and thermodynamic barriers' imposed by the media [35].

Fig. 1 shows cyclic voltammograms of $\mathrm{AuCl_4^-}$ in DMSO. In the figure, $\mathrm{P_1}$ and $\mathrm{P_2}$ correspond to the reactions (3) and (4), respectively. Each cycle shown in the figure is the first scan recorded in separated experiments, after the surface of the electrode was previously polished. It can be noted that after the surface has been polished the formation of the intermediate in solution, $\mathrm{P_1}$, is reproducible. On the contrary, the formation of metallic gold, $\mathrm{P_2}$, is not. This fact indicates that the electroreduction of $\mathrm{AuCl_2^-}$ to metallic gold is highly dependent on the surface morphology of the polycrystalline working electrode. Moreover it has been reported that it also depends on the electrode material [22]. In the reverse scan, the cathodic peak $\mathrm{P_3}$ shows the reactivation of the electrode. In general, this happens when inhibitory species are removed from the surface leaving the electrode exposed again to more gold electrodeposition, at potentials, where the electrodeposition of gold is still favourable. Contrary to what one might expect, $\mathrm{P_4}$ has been assigned to the oxidation of $\mathrm{Cl^-}$ to $\mathrm{Cl_2}$ rather than to the formation of $\mathrm{AuCl_2^-}$ or $\mathrm{AuCl_4^-}$, given that similar anodic peaks were recorded with solutions containing only $\mathrm{Cl^-}$, at glassy carbon electrodes [36]. The stripping of gold to produce gold chloride complexes takes place at much larger anodic overpotentials [21,22]. The inset of the figure shows the voltammetric response obtained in the ionic liquid $\mathrm{TBMA^+NTf_2^-}$. Although the voltamograms recorded in DMSO and in $\mathrm{TBMA^+NTf_2^-}$ are quite similar, the magnitude of the current in the later case is considerably smaller. This is related to the high viscosity of the medium [37,38].

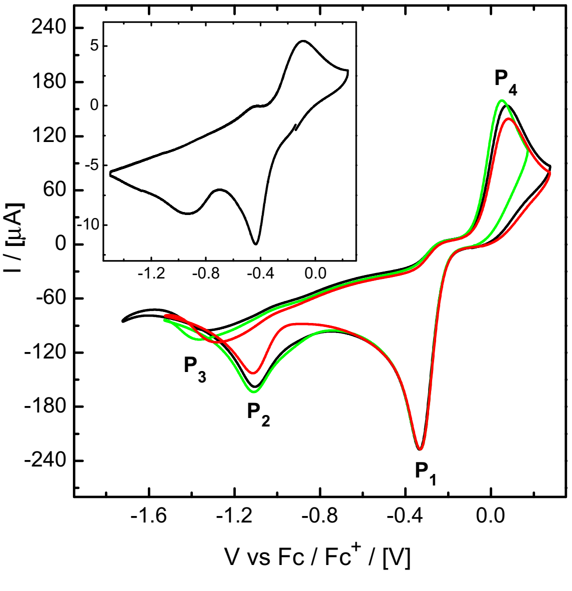

Fig. 1. Cyclic voltammograms for the reduction of $\mathrm{AuCl_4^-}$ in DMSO. In the figure are the first cycles recorded in separated experiments. Electrochemical reduction takes place in two steps: at ∼−0.3 V $\mathrm{AuCl_4^-}$ reduces to $\mathrm{AuCl_2^-}$ ($\mathrm{P_1}$) and at ∼−1.1 V $\mathrm{AuCl_2^-}$ reduces to $Au_{(0)}$ ($\mathrm{P_2}$). Experimental conditions: 5 mM $\mathrm{KAuCl_4}$, 0.1 M $\mathrm{KClO_4}$, v = 50 mV s^{-1}. Inset: Cyclic voltammogram for the reduction of 5 mM $\mathrm{AuCl_4^-}$ recorded in the ionic liquid $\mathrm{TBMA^+NTf_2^-}$. v = 50 mV s^{-1}. Working electrode: polycrystalline gold disc electrode, 5 mm diameter.