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Underpotential deposition of silver on gold from deep eutectic electrolytes

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ABSTRACT

The electrochemical behavior of Ag(I) in choline chloride-urea medium (ChCl-U) has been investigated at a gold electrode using cyclic voltammetry. Cyclic voltammograms revealed a diffusion limited reduction wave coupled on the reverse sweep with an oxidation wave that corresponds to the dissolution of a bulk deposit. Beside these main peaks, we have highlighted other peaks at potentials more positive than the thermodynamic potential of silver bulk deposition. Experiments at various potential scan rates have indicated that, contrary to the main reduction peak, these peaks are indicative of a surface process that corresponds to an underpotential deposition (upd) of silver. The absence of upd at glassy carbon or platinum electrodes in ChCl-U has ruled out the influence of silver speciation on the existence of the upd process. The occurrence of silver upd on gold is moreover not linked to the nature of the H-bond donor (urea, ethylene glycol or oxalic acid) of the choline choride DES.

1. Introduction

Deep Eutectic Solvents (DESs) have been introduced for the first time by Abbott et al. in 2003 [1]. DESs share many features and benefits with ionic liquids (ILs), their cost is however much lower so that they are presently considered as promising alternatives to conventional solvents for a large number of applications. These solvents are usually prepared by mixing a quaternary ammonium salt with a hydrogen-bond donor, leading to a melting point much lower than the pure components. Smith and co-workers have recently reviewed the properties of DESs, their applications, among which the electrodeposition of metals [2]. The review highlights the wide range of applications but also shows a cruel lack of fundamental studies on electrodeposition in DESs.

In this work we investigate a system that has been extensively documented in aqueous media i.e. the electrodeposition of silver on gold. Owing to their excellent electrical characteristics, silver deposits are indeed of great importance for the electronics industry. Silver plating is usually performed by electrodeposition from conventional aqueous silver baths that contain cyanides and are thus highly toxic. To avoid the use of cyanide, different alternatives in aqueous media are investigated, but it remains still difficult to achieve a good performance (quality of deposit and solution stability) with cyanide-free electrolytic solutions [3–5].

To satisfy sustainable requirements, non-conventional electrolytes such as DESs appear as good candidates for electrochemical deposition of metals [6], owing to their high thermal stability, wide electrochemical window, high electrical conductivity, good air and water stabilities, and high capability to dissolve metal salts [2,7]. Various data on silver electrodeposition from DESs made of choline chloride (ChCl) with either urea (U) or ethylene glycol (EG) are already available. The deposition of silver on copper [8–11], carbon [12,13], platinum [9,11,14–17] and gold [9,16,18,19] substrates has been investigated using various techniques. On copper, an electroless mechanism was evidenced in ChCl-EG which, unlike in aqueous media, does not stop after the deposition of a monolayer of silver, but produces a layer of several micrometers due to the high porosity of the deposit [8,9]. On carbon, using cyclic voltammetry and chronoamperometry, Sebastián et al. [12,13] have compared the nucleation and the growth of the silver deposit from aqueous and deep eutectic solvents. Abbott et al. [14] have reported for the first time the deposition of silver on platinum from a ChCl-U electrolyte. In order to improve the resistance of the silver deposited film, the use of additives (SiC, Al_2O_3 and LiF) to the ChCl-U silver bath [15] was also considered. Recently, Abbott et al. also investigated the silver deposition with the use of an electrochemical quartz crystal covered with a gold film in order to quantify the deposition yield [16] and to study the nucleation and growth

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process by a Digital Holographic Microscopy technique (DHM) [19]. These contributions also demonstrated the influence of hydrogen bond donors either EG or U on the growth of the silver deposit that was found to proceed by a 3D nucleation coupled with a diffusion control.

In the present work, the electrochemical behavior of Ag(I) species in ChCl-U at gold electrodes was further investigated with special emphasis on two-dimensional deposition that may take place at potentials more positive than those thermodynamically required for bulk deposition. Evidence for the occurrence of underpotential deposition (upd) of silver on gold from deep eutectic solvents is, to our knowledge, provided here for the first time.

2. Experimental

2.1. Reagents

Purification of choline chloride and drying of the chemicals were found to markedly improve the reproducibility of the voltammetric experiments. Choline chloride (Alfa Aesar, 98 +%) was purified by recrystallization in absolute ethanol (VWR Chemicals, NORMAPUR), filtered and dried under vacuum. Urea (VWR Chemicals, NORMAPUR) and oxalic acid dihydrate (VWR Chemicals, NORMAPUR) were used without further purification and stored in a desiccator to avoid the absorption of moisture. Silver chloride (Alfa Aesar, 99.9%), ethylene glycol (EMSURE, analytical grade), sodium chloride (VWR Chemicals, NORMAPUR) and perchloric acid (Merck, Suprapur) were used as received.

2.2. Deep eutectic solvent preparation

The DESs were obtained by mixing the constituents under constant stirring for 3 hours at 60 °C. Choline chloride and urea were mixed in a 1:2 molar ratio in a closed container to form the ChCl-U DES while choline chloride and ethylene glycol were mixed in a 1:1 ratio to form the ChCl-EG DES. The ChCl-Ox DES was produced in an open container containing choline chloride and oxalic acid in a 1:2 molar ratio. In all cases, the AgCl salt was added directly at the beginning of the DES preparation. Silver concentrations are expressed in molalities (mol of Ag per mass of DES). At 60 °C, a concentration of 25 mmolal equals to 29.4 mM. The water content of ChCl-U and ChCl-EG determined by Karl Fisher titration (Mitsubishi, MCI Model VA-05), were typically less than 1000 ppm.

2.3. Electrochemical experiments

The electrochemical experiments were carried out using a three electrode system connected to an Autolab PGSTAT20 (Metrohm) potentiostat. The working electrodes were either gold (BASi, geometric area = 0.0201 cm^2), platinum (BASi, geometric area = 0.0201 cm^2) or glassy carbon (BASi, geometric area = 0.0707 cm^2) discs and the counter electrode was a platinum grid of large area. For the rotating disc electrode (RDE) experiments, a gold disc electrode (EDI 101 Radiometer Analytical, geometric area = 0.0314 cm^2) was employed. The rotation rate was controlled by a Speed Control Unit (Radiometer Analytical CTV101). The real area of the gold electrodes was estimated from the charge involved in the formation/dissolution of one oxide monolayer in 0.1 M perchloric acid [20], yielding typical roughness factors of the order of 2.5. In the literature, a silver wire pseudo reference is usually employed in DESs but its equilibrium potential depends on the actual silver concentration. In addition, ferrocene cannot be used to calibrate the pseudo reference because it is not soluble in ChCl-U [21,22]. For these reasons, a home-built reference electrode was used, separated from the electrolyte medium with the help of a Vycor® glass tube. This reference was made from ChCl–U containing a concentration of 10 mmolal of AgCl and stored in an oven at 60 °C. It corresponds to the half-cell Ag|AgCl (ChCl-U, $m = 10\ \mathrm{mmol\ kg^{-1}}$), which will be hereafter shortly written as Ag(I)/Ag. The working electrodes were polished with a 1.0 μm alumina-water slurry on a smooth polishing cloth (Struers), then twice sonicated for 3 minutes and rinsed with Milli-Q water to remove any trace of alumina, and finally dried under nitrogen. The platinum counter electrode was cleaned by flaming to red glow. Before each experiment, the DES was purged with nitrogen for at least 20 min, and kept during all measurements under nitrogen atmosphere, except for the ChCl-Ox for which no nitrogen bubbling was used in order to achieve better reproducibility. Prior to use, all glassware was cleaned with Milli-Q water and dried in an oven.

3. Results and discussion

Cyclic voltammogramms (CV) recorded in ChCl-U containing 25 mmolal of AgCl at a gold electrode in a temperature range from 40 °C to 70 °C are shown in Fig. 1. The electrochemical response of the Ag(I) species is clearly evidenced in the accessible potential window of the Au/ChCl-U system, with the CV exhibiting a reduction wave coupled with an oxidation wave on the reverse sweep. The cathodic peak at negative potentials is associated with the reduction of Ag(I). On the reverse scan, the dissolution of the silver deposit starts near −0.08 V. When the temperature increases, two trends are observed. The first one is a shift of the anodic peak in the negative direction, whereas the cathodic peak position is barely influenced. The second one is an increase in the intensities of the anodic and cathodic peaks, consistent with the decrease of the electrolyte viscosity resulting in a more efficient mass transport. According to published data [23], the viscosity decreases drastically from 20 °C to 60 °C (from 1372.0 to 68.7 mPa s, respectively), while the diminution is only from 68.7 to 42.0 mPa s between 60 °C and 70 °C so that a working temperature of 60 °C was selected for the present study.

The influence of the silver salt concentration on the CV curves revealed a linear relation between the cathodic peak current and the silver concentration in the range of 10 to 50 mmolal of AgCl. In the present work, a concentration of 25 mmolal AgCl was chosen.

Fig. 2 highlights the impact of three different electrode materials on the voltammetric response of silver in ChCl-U. The CV curve recorded at the gold electrode does not exhibit the typical feature associated with a kinetic control by nucleation and growth

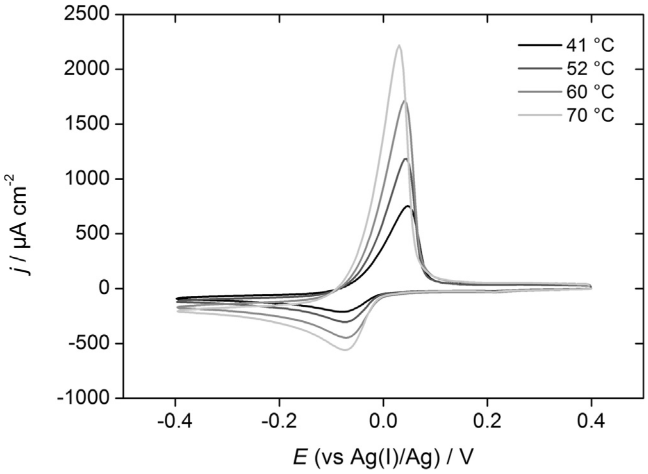

Fig. 1. Cyclic voltammograms (first scan) of ChCl-U with 25 mmolal of AgCl at various temperatures as indicated in the legend. Scan rate = 20 mV s^{-1}.