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Unusual electrochemical behaviour of $AuBr_4^-$ in ionic liquids. Towards a simple recovery of gold(III) after extraction into an ionic liquid.

Nicolas Papaiconomou*[a,b,c], Nicolas Glandut[d], Isabelle Billard[c,e,f] and Eric Chainet[b,c]

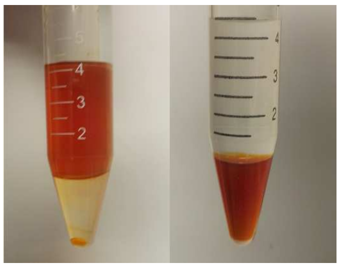


Fig. 1 - Snapshots of $AuBr_4^-$ extraction using [C_8PYR][NTf_2]. First snapshot on the left : aqueous solutions of $AuBr_4^-$ over [C_8PYR][NTf_2]. Second snapshot: same system after 1 min of gentle shaking. The orange colour in the lower phase corresponds to $AuBr_4^-$ anions extracted towards the ionic liquid phase.

Abstract

The electrochemistry of $AuBr_4^-$ complexes extracted towards ionic liquids [C_8PYR][NTf_2] or [C_8MIM][NTf_2] saturated with water and gas has been studied by cyclic voltammetry on macro electrodes and by linear voltammetry on a platinum microelectrode. Unlike $AuCl_4^-$, the reduction of $AuBr_4^-$ to Au(0) is achieved following a one reduction step involving three electrons. The deposition of Au(0) from $AuBr_4^-$ is carried out at a potential above that of water, leading to the simple and easy deposition of gold subsequently to the extraction of $AuBr_4^-$ towards an ionic liquid.

Introduction

The extraction of $AuCl_4^-$ or $AuBr_4^-$ anions from water using ionic liquids has been recently reported by our group.[1] The distribution coefficients obtained are very high, yielding quantitative extraction of gold towards an ionic liquid (IL) phase. Using such phases is interesting from an environmental point of view because ionic liquids are not flammable and exhibit very low vapour pressure. Furthermore, the method proposed in our previous paper does not involve any cyanide compounds.

Nevertheless, a successful gold extraction process necessarily needs to achieve not only high distribution coefficients, but also to provide a facile and energetically favourable recovery of gold from the extracting phase.

Previous reports have studied the electrochemical behaviour of tetrachloroaurate(III) complexes in neat ionic liquids, revealing a two-steps reduction of Au(III) towards Au(I) and Au(0). However, no study so far has reported the electrochemistry of another interesting gold(III) complex anion, namely $AuBr_4^-$, within an ionic liquid.

The objectives of this article are first to study the electrochemistry of $AuBr_4^-$ in ionic liquids and compare it to that of $AuCl_4^-$ species and second to investigate on a simple process for the recovery of gold(III) from an ionic liquid subsequently to the extraction of $AuBr_4^-$ towards an ionic liquid.

To that end, electrochemistry of $AuBr_4^-$ in 1-octylpyridinium bis(trifluoromethanesulfonyl)imide ([C_8PYR][NTf_2]) and 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_8MIM][NTf_2]) is reported here. [C_8PYR][NTf_2] was chosen because high distribution coefficients for $AuBr_4^-$ in this ionic liquid were obtained and because it is known to exhibit a water-content lower than those of other ionic liquids such as those based on imidazolium for instance.[2,3] [C_8MIM][NTf_2] was chosen because it is a member of the most studied family of ionic liquids in the literature. In addition, using this ionic liquid allowed comparison of our results with those previously reported for the voltammetric study of $AuCl_4^-$ in [C_4MIM][NTf_2] (1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide).[4,5,6]

To the best of our knowledge, we are the first to carry out such experiments using $AuBr_4^-$ dissolved in an ionic liquid without any preliminary degassing and drying of the IL. This liquid medium, referred to as "wet" ionic liquid, is therefore saturated in water and gases (O_2, N_2, CO_2, etc) throughout the electrochemical study of gold.

Experimental section

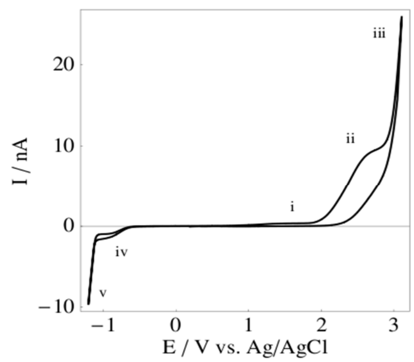
Extraction experiments were carried out contacting 0.75 mL of [C_8PYR][NTf_2] with 4 mL of a pH 1 aqueous solution of HCl or HBr accordingly and containing 2.5 mM $KAuCl_4$. The tube was left on a shaker for 24 hours and centrifuged at 3000 g for 30 min. Analysis of the aqueous phases prior and after extraction was carried out with the help of an ICP-MS apparatus from Agilent.

UV-Vis spectra were recorded on a Cary 50 UV-Vis spectrophotometer from Varian.

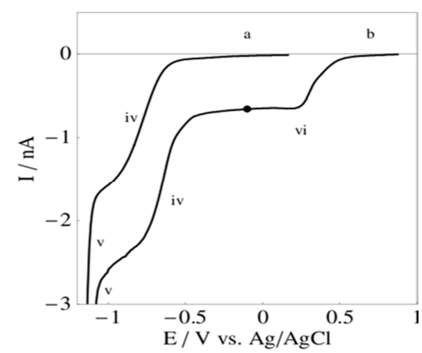
Electrochemistry was carried out at room temperature (25 °C) in a standard three-electrode cell configuration. An Autolab PGSTAT30 potentiostat was used, controlled by GPES 4.9 software (EcoChemie, The Netherlands). For both deposition and stripping experiments, the working electrode (WE) was a 10 µm diameter platinum microelectrode (ALS, Japan), and the counter electrode (CE) was a platinum coil (ALS). For deposition, the solution was the [C_8PYR] [NTf_2] ionic liquid, and a silver wire covered with silver chloride (Ag/AgCl ; Radiometer-Analytical, France) was used as a quasi-reference electrode. For stripping, the solution was a 0.5 M HCl aqueous solution (Aldrich and Millipore MilliQ+ water), and the reference electrode was a saturated calomel electrode

(SCE; ALS). Acetone (min. 99.8 %; VWR), ethanol (min. 96 %; VWR) and deionized water (MilliQ+, 18.2 MΩ cm resistivity) were used for rinsing the WE and the CE between deposition and stripping experiments.

Fig. 2 Cyclic



voltammogram of "wet" [C_8PYR][NTf_2] ionic liquid. T = 25 °C. Scan rate 10 mV.s^{-1} . Pt



microelectrode, diameter 10 µm.

Fig. 3 - Cathodic linear sweep voltammograms in "wet" [C_8PYR] [NTf_2] (a) in the absence, and (b) in presence of 17.2 mM $AuBr_4^-$. Dot at −0.1 V indicates where gold deposition was done by chronoamperometry.

Cyclic voltamperometric experiments were recorded on a Versastat 3F potentiostat from Princeton Research using a custom made 1 mL thermostated electrochemical cell. Working electrode was a 5 mm glassy carbon (GC) electrode. Reference electrode was either a silver wire covered with AgCl or AgBr, or a bare silver wire. Counter electrode was a glassy carbon cloth.

Anodisation of gold was carried out using a gold wire as a working electrode together with a platinum counter electrode and a Ag wire pseudo-reference in a three-electrode set up. In order to avoid any oxydation of the ionic liquid, anodisation of gold was carried out at a potential of 1.5 V vs. Ag for 36 hours.

Results and discussions

Extraction of gold within an ionic liquid

The procedure for the extraction of $AuCl_4^-$ or $AuBr_4^-$ was reported previously[1] and will thus be only briefly recalled. At pH 1, distribution coefficients for $AuCl_4^-$ extracted towards [C_8MIM][NTf_2] was found to be 520, as reported previously. Distribution coefficients of 6600 and 34000 were obtained for $AuBr_4^-$ extracted towards [C_8PYR][NTf_2] and [C_8MIM][NTf_2], respectively. Fig. 1 shows snapshots taken prior and after the extraction of $AuBr_4^-$ was carried out.

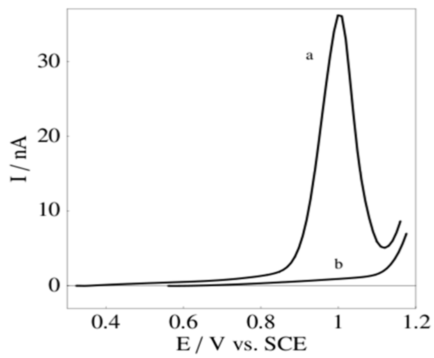
After extraction of $AuBr_4^-$ in [C_8MIM][NTf_2] or [C_8PYR][NTf_2], the ionic liquid phases exhibited a dark orange colour. The UV-Vis spectrum of the ionic liquid phase was found to be very similar to that of $AuBr_4^-$ in water.[7] Maximum absorption wavelength values of 380 and 398 nm for $AuBr_4^-$ in water and [C_8MIM][NTf_2] or [C_8MIM][NTf_2] were obtained respectively. The small bathochromic shift observed is due to the influence of the ionic liquid cations surrounding $AuBr_4^-$ anion.[8]

Reduction of $AuBr_4^-$ using a micro-electrode

In a preliminary step, the electrochemistry of [C_8PYR][NTf_2] on a microelectrode was investigated. The electrochemical window of a 10-µm diameter Pt microelectrode in a dried sample of [C_8PYR][NTf_2] not containing any gold was recorded as shown in Fig. 2. The electrochemical window is in good agreement with previous reports dealing with ionic liquids based on alkylpyridinium cations.[9,10] The reduction of 1-octylpyridinium occurs at a potential slightly below -1 V vs. Ag/AgCl. A window of approximately 3 V is available for performing electrochemical deposition of metals. Five voltammetric waves, named i to v, can be observed. Three are in oxidation, and two in reduction. Wave i, which is very small, could be due to oxidation of traces of water or of Br− ions resulting from the synthesis procedure. Wave ii is a prewave before oxidation of the IL, and could be attributed to Pt electrode oxidation.[2] Wave iii is the oxidation of the IL, especially of its [NTf_2] anion. Wave iv is a prewave before reduction of the IL, and could be due to reduction of water traces. To finish, wave v is the reduction of the IL, especially of its [C_8PYR]$^+$ cation. No reduction wave that could have been attributed to reduction of surface Pt oxides, is visible. This is perhaps the sign that soluble Pt cations are produced, and that they diffuse away from the electrode. This corrosion would not be surprising, because ca. 3 V potentials are reached. The exact knowledge of the reactions occurring in waves ii and iii are not the scope of this article. Moreover, gold electrodeposition will be carried out in a potential range where none of reactions i to v occur.

Electrodeposition of gold in [C_8PYR][NTf_2] subsequent to its extraction from water was then carried out in the most simple manner. After the ionic liquid phase was removed from the tube in which the extraction experiments had been carried out, microelectrodes were directly inserted into the dark orange ionic liquid. We insist here on the fact that neither drying nor degassing of the ionic liquid phase in any form was carried out prior to the electrodeposition experiments.

Fig. 4 - LSVs Anodic of Pt



microelectrode in aqueous 0.5 M HCl; (a) bare; (b) covered by gold after 100-second deposition in [C_8PYR] [NTf_2] at −0.1 V vs. Ag/AgCl. T = 25 °C. Scan rate 50 mV.s−1 . Pt microelectrode, diameter 10 µm.

Fig. 3 shows linear sweep voltammograms (LSVs) in reduction, of a Pt microelectrode in [C_8PYR][NTf_2], in the absence (a) and in presence (b) of $AuBr_4^-$ anions. Waves iv and v shown in Fig. 3 are visible in both cases. In presence of $AuBr_4^-$, an additional wave of reduction, named vi, appears. It features a simple S shape, characteristic of a one-step, first-order electrochemical reaction occurring at a microelectrode.[11] Wave vi is attributed to the reduction of $AuBr_4^-$ into gold metal[12,13] or to the formation of $AuBr_2^-$:[11]

$$AuBr_4^- + 3e^- \rightarrow Au + 4Br^- \text{(peak vi and xi)} \qquad (1)$$

$$AuBr_4^- + 2e^- \rightarrow AuBr_2^- + 2Br^- [0.564\, V/SCE] \qquad (2)$$

Eqn (2) is however excluded by the following results. First, a 100-second chronoamperometry at a fixed potential of −0.1 V vs. Ag/AgCl, has been performed (see dot, Fig. 3b). After this, the electrode was removed from the cell containing the ionic liquid, and was rinsed thoroughly with first acetone, then ethanol, and to finish deionized water, at least 20 seconds each. The micro-electrode was then immediately plunged into an aqueous solution containing 0.5 M HCl. Stripping of gold presumably deposited was carried out from 0.3 to 1.2 V / SCE. The corresponding voltammogram is presented in Fig. 4, curve a. The perfectly symmetrical peak, which is consistent with surface oxidative stripping of a metal, is centred around 1.00 V / SCE and exhibits a peak value of ca. 35 nA. The value for the potential of the stripping peak (1.00 V / SCE) is in very good agreement with previous works reporting the stripping of gold in aqueous solutions containing HCl.[15-17] Furthermore, because $AuBr_2^-$ formed following eqn (2) would have been washed out during the rinsing procedure, and because an important stripping peak obtained in Fig. 4 is related to the formation of a significant amount of Au on the microelectrode, we can conclude that the reduction of gold follows quantitatively eqn (1) and not eqn (2).

The expression of the limiting plateau current at a disk microelectrode is given by:[11]

$$I_{\text{Lim}} = -4nFDcr \qquad (3)$$

where n = 3 is the number of electrons involved in eqn (1), F = 96 485.3 C is the Faraday constant, r = 5 µm is the radius, D the diffusion coefficient of $AuBr_4^-$ species, and c their bulk concentration. Knowing the bulk concentration (c = 17.2 mM) and the limiting plateau current measured here (I_{lim} = −0.66 nA) from Fig. 4, the diffusion coefficient of $AuBr_4^-$ in [C_8PYR][NTf_2], D, could be determined. The value of 6.6 × 10^{-8} $cm^2.s^{-1}$ calculated here is in very good agreement with that of $AuCl_4^-$ (D = 5.2 10-8 cm².s⁻ ¹) found in the literature.[5]
During the 100-second chronoamperometry at a fixed potential of −0.1 V vs. Ag/AgCl mentioned above, ca. 90 nC were used. Ca. 70 nC were obtained by integrating under the stripping peak (with background correction) shown in Fig. 5. Gold metal is known to oxidise as follows[12-14] in presence of chloride anions:

$$Au + 4Cl^- \rightarrow AuCl_4^- + 3e^- \qquad (4)$$

and

$$Au + 2Cl^- \rightarrow AuCl_2^- + e^- \qquad (5)$$

Previous results have shown that because of eqns (4) and (5), 1.9 electrons per atom of gold was obtained for the stripping of gold in water containing HCl.[15] According to eqn (1), the 90 nC obtained during the deposition step correspond to the reduction of 3.1 10^{-13} mol of gold. Since 70 nC are obtained during the stripping of 3.1 10^{-13} mol of gold, we can conclude that 2.3 electrons are produced per gold atom stripped to the aqueous solution. This value is indeed close to the value of 1.9 electrons previously reported.[15]

Finally, the bare Pt microelectrode was rinsed in the same way, i.e, with acetone, ethanol and water. No peak at 1.0 V / SCE can be seen (Fig. 4b). This confirms that the peak observed at 1 V is due to Au metal stripping, and not to platinum oxides, acetone or ethanol. This confirms that gold was indeed deposited on the microelectrode using [C_8PYR][NTf_2].

Cyclic voltammetry of AuX_4^- (X = Cl^-, Br^-)

In order to gain a better understanding at the electrochemical processes occurring for gold complexes in a so-called wet ionic liquid and to compare with previous reports, cyclic voltammetry of $AuCl_4^-$ or $AuBr_4^-$ extracted within ionic liquid [C_8MIM][NTf_2] was carried out.
In a preliminary step, the electrochemistry of so-called "wet" [C_8MIM][NTf_2] was studied on a glassy carbon electrode. The corresponding voltammogram is plotted in Fig. 5 (curve with long dashes) and shows reduction peak vii centred around -0.75 V vs. Ag/AgCl. This peak is due to the reduction of water or acid dissolved within the ionic liquid.
The electrochemical study of [$AuCl_4^-$] in wet [C_8MIM][NTf_2] was then carried out in order to compare our results with those previously obtained for the same gold complex ion dissolved in neat [C_4MIM][NTf_2] (1-methyl-3-butylimidazolium bis(trifluoromethanesulfonylimide) as reported elsewhere.[6]

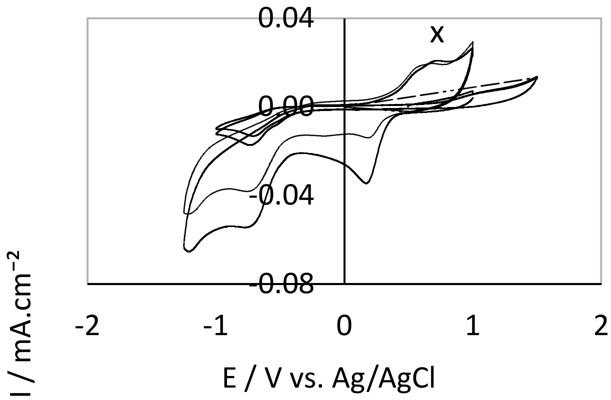


Fig. 5 - Cyclic voltammogram of $AuCl_4^-$ dissolved in $[C_8MIM][NTf_2]$ and recorded on a GC electrode. Scan rate : $50 mV.s^{-1}$.

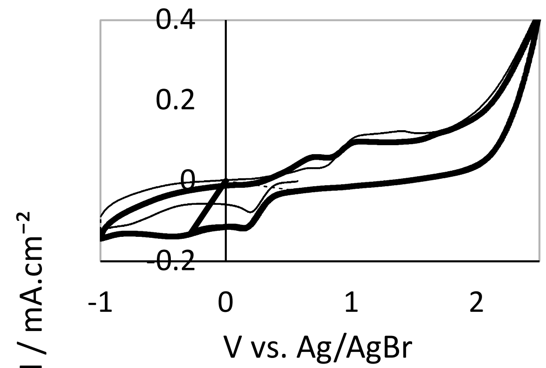


Fig. 6 - Cyclic voltamperograms of $AuBr_4^-$ in $[C_8MIM][NTf_2]$ displaying first (- -) and second (—) cycles using a GC electrode and a scan rate of 250 mV. s^{-1}.

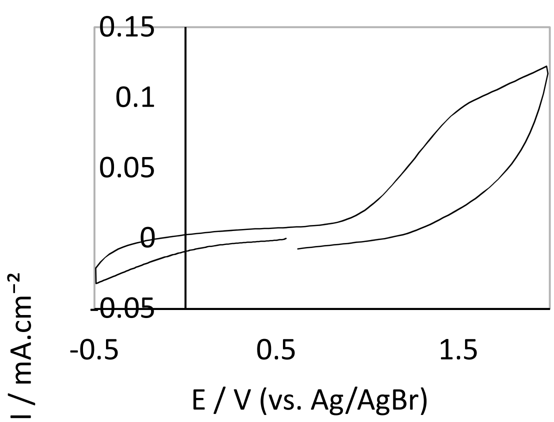


Fig. 7 - Cyclic voltammograms of $[C_8MIM][Br]$ dissolved in $[C_8MIM][NTf_2]$ using a GC electrode and a scan rate of 50 mV. s^{-1}.

As shown in Fig. 5, three reduction peaks, referred to as vii (-0.75 V), viii (0.20 V) and ix (-0.95 V) can be observed. According to ref. 16, the two peaks viii and ix correspond to the reduction steps of $AuCl_4^-$ to $AuCl_2^-$ and $AuCl_2^-$ to Au(0):

$$AuCl_4^- + 2e^- \rightarrow AuCl_2^- + 2Cl^- \text{(peak vii)} \quad (6)$$

$$AuCl_2^- + 1e^- \rightarrow Au + 2Cl^- \text{(peak ix)} \quad (7)$$

The shift in the reduction potentials between those obtained here and those previously reported are due to the difference in nature of the ionic liquid cation (octyl vs. butyl chain length on the imidazolium cation). Also notice that the potentials reported here are vs. Ag/AgCl and not Ag/Ag^+. This result proves that deposition of gold after $AuCl_4^-$ is extracted into an IL is only possible at the expense of a significant energetic cost because water will be reduced simultaneously with gold.
Peak x that is to be seen on Fig. 5, again according to ref. 16, corresponds to the oxidation of chloride ions from the gold complex $AuCl_4^-$.
The cyclic voltammogram of $AuBr_4^-$ in $[C_8MIM][NTf_2]$ recorded between -1 and 2 V vs. Ag/AgBr reference electrode and at a scan rate of 50 $mV.s^{-1}$ is shown in Fig. 6. Unlike what was observed for $AuCl_4^-$, and in agreement with our present results obtained using a micro-electrode, only one reduction peak (peak xi) occurred at + 0.20 mV on the first cycle, which is attributed to the reduction of Au(III) to Au(0) as shown in eqn. 1. Again, the slight difference in reduction potential obtained in the preceding section and that reported here is due to the different nature of ionic liquid used ($[C_8MIM][NTf_2]$ vs. $[C_8PYR][NTf_2]$). Peak xii (- 0.95 V) present at the extreme left of the voltamperogram is due to the reduction of water. During the second cycle, peak xii was found to move to higher potentials (-0.45 V). This is due to the fact that as a thin layer of gold is deposited on the GC electrode during the first cycle, the working electrode can be considered as a gold electrode during the second cycle. The reduction of water (or of H^+ ions) will thus occur at higher potentials, in agreement with the results presented in ref. 6.
Fig. 6 also shows two oxidation peaks (xiii and xiv). Because such peaks did not occur in Fig. 5, investigation was carried out by studying a solution of $[C_8MIM][NTf_2]$ containing approximately 1 mM of $[C_8MIM][Br]$. The cyclic voltammogram carried out under the same conditions as those detailed above did not yield any reduction nor oxidation peaks below 1 V (Fig. 7). The oxidation and reduction of bromide anion was therefore excluded. Moreover, it can be stated that the oxidation peaks observed in Fig. 6 are related to the presence of gold in the ionic liquid.
To gain further insights into the oxidation peaks found in Fig. 6, a cyclic voltammogram of gold in $[C_8MIM][NTf_2]$ without any chloride anion present in the solution was also recorded. To that end, gold was anodized within $[C_8MIM][NTf_2]$ as detailed in the experimental section. In order to avoid any oxidation of the ionic liquid during the process, the oxidation of gold in $[C_8MIM][NTf_2]$ was carried out at 1 V. At that voltage, the phenomenon appears to be rather slow, and because no quartz micro-balance could be used in the course of the experiment, no precise concentration of gold in $[C_8MIM][NTf_2]$ was determined. Despite this, performing cyclic voltammetry on the solution obtained after oxidation of gold within $[C_8MIM][NTf_2]$ under the same conditions as detailed above (i.e., glassy carbon working electrode, platinum counter electrode and a silver wire as a pseudo-reference electrode), a well defined reduction peak (peak xv)

at -0.90 V was observed, as shown in Fig. 8. Surprisingly, no oxidation peak was observed, even up to 2 V. This confirmed that the oxidation peak xiii and xiv of Fig. 6 are due to the oxidation of gold complexed with bromide ions. To further confirm this assumption, [C_8MIM][Br] was added to the solution of anodized gold in [C_8MIM][NTf_2]. After stirring the solution for 5 minutes, a cyclic voltammogram was recorded as plotted in Fig. 8. The two well-defined oxidation immediately appeared, further confirming that these peaks are due to the oxidation of Au(0) into Au(I) and Au(III) complexed with Br^- anions. Peaks xiii and xiv are thus expected to correspond respectively to the equations

$$Au + 2Br^- \rightarrow AuBr_2^- + 1e^- \text{(peak xiii)} \quad (6)$$

$$Au + 4Br^- \rightarrow AuBr_4^- + 3e^- \text{(peak xiv)} \quad (7)$$

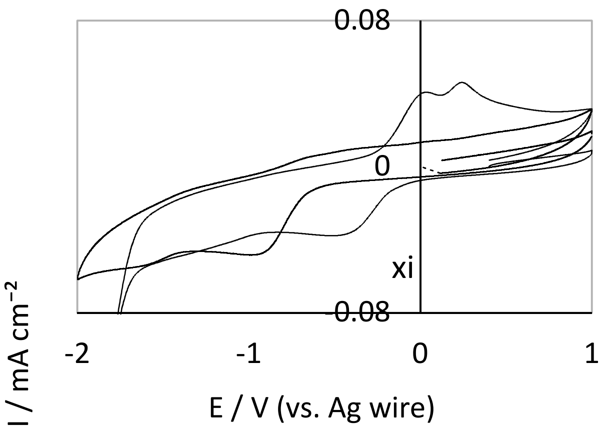


Fig. 8 - Cyclic voltamperograms of gold once anodized in [C_8MIM][NTf_2] prior (---) and after (...) addition of [C_8MIM][Br] using a GC electrode and a scan rate of 50 mV. s^{-1}.

Conclusions

These preliminary results demonstrate that ionic liquids can be used in the development of greener alternative processes not requiring preprocessing treatments, such as drying or degassing, for the recovery of precious metals such as gold. $AuBr_4^-$ appears to be reduced to elemental gold in a one-step reduction process at a potential higher than that of water in "wet" and not degassed ionic liquids [C_8PYR][NTf_2] or [C_8MIM][NTf_2]. Cyclic voltammetry has provided better understanding of the electrochemistry of $AuBr_4^-$ dissolved in a wet and not degassed ionic liquid.

Therefore, electrochemical recovery of gold starting from $AuBr_4^-$ instead of $AuCl_4^-$ is possible, exhibiting extremely high distribution coefficients and very easy recovery of elemental gold metal.

A thorough investigation of the competitive extraction of gold in presence of other metals such as platinum, iron, nickel or copper, and the electrochemical deposition of the extracted metals will be the subject of a subsequent work.

Notes and references

[a] *Univ. Savoie, LEPMI, F-73000, Chambéry, France.*
[b] *Univ. Grenoble-Alpes, LEPMI, F-38000, Grenoble, France.*
[c] *CNRS, LEPMI, F-38000, Grenoble, France.*
[d] *SPCTS, UMR 7315, CNRS, University of Limoges, European Ceramics Center, France. E-mail: nicolas.glandut@unilim.fr*
[e] *Université de Strasbourg, IPHC, 23 rue du Loess, 67037 Strasbourg, France..Tel: +33 388106401; E-mail: isabelle.billard@iphc.cnrs.fr*
[f] *CNRS, UMR 7178, 67037 Strasbourg, France*

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