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# Voltammetric and in situ FTIRS study on $\text{CN}^-$ and $\text{Au}(\text{CN})_x^-$ complexes at the polycrystalline gold surface in citrate medium

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## Abstract

The adsorption and reactivity of citrate anions, cyanide anions, and the Au(I) and Au(III) cyanocomplexes ( $\text{KAu}(\text{CN})_2$  and  $\text{KAu}(\text{CN})_4$ , respectively) on gold polycrystalline electrodes have been investigated by means of cyclic voltammetry and in situ FTIR spectroscopy in pH 7 sodium citrate medium. It was found that citrate anion adsorbs reversibly through the carboxylate groups from 0.4 V (RHE) on bare gold surfaces. However, the onset of this adsorption process is shifted by 600 mV in the positive direction when adsorbed cyanide species are present at the electrode surface. The Au(I) cyanocomplex produces a film on the gold electrode that inhibits the oxidation of both citrate anions and the gold surface. The reduction of the Au(III) cyanocomplex gives rise to the formation of the Au(I) cyanocomplex at potentials less negative than those required for gold deposition. Upon reduction, both cyanocomplexes release adsorbed cyanide on the gold electrode, which can be subsequently oxidized to cyanate at higher potentials. © 2004 Published by Elsevier B.V.

**Keywords:** Citrate; Gold; FTIR spectroscopy; Gold cyanocomplex; Cyclic voltammetry

## 1. Introduction

Electrodeposition of Au and its alloys is a niche in applied metal electrochemistry with a remarkable commercial background in the electronic, electric, jewellery and fashion industries. Typical industrial plating processes are carried out with cyanoalkaline solutions containing free cyanide. Neutral and acidic baths based on Au(I) and Au(III) cyanocomplexes and not containing free cyanide incur industrial interest mainly for environmental and personnel safety reasons. Some patents and proven processes are available, but their implementation at the production level is impaired chiefly by difficulties in controlling the plating process. At this stage of the knowledge of these systems, industrial development issues call for fundamental understanding of several of both the cathodic and anodic aspects of the

electroplating process. In particular, the use of organic additives in the electrodeposition of Au from neutral  $\text{Au}(\text{CN})_2^-$  baths and acidic  $\text{Au}(\text{CN})_4^-$  solutions has notable effects on the structural, mechanical and morphological properties of the deposit. The understanding of the electrochemical deposition of gold is of both technological and fundamental importance. Extensive efforts have been made toward the understanding of the electrochemical and chemical behaviour involved in the gold deposition process and the gold deposits formed [1,2]. The optimisation of organic additives for metal plating strongly needs an electrochemical approach at the molecular level. In situ Fourier transform infrared spectroscopy (FTIR) is the method of choice for such an approach in terms of quantitative capability and surface sensitivity.

The technological relevance of both citrate and citric acid in the field of electroplating processes is testified by their wide use as additives for the electrodeposition baths of several (mainly transition) metals and their alloys [3–9]. Electrochemical studies have, so far, focussed

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mainly on the reduction kinetics of the metal ions in the presence of citrate in the deposition bath [8]. A complexing action is accepted of citrate towards metal ions in the solution, enhancing cathodic polarisation [9]. In particular, a specific effect of the presence of citrate has been observed on the composition of electrodeposited alloys such as Sn–Mn, Ni–Fe [5], Ni–W [10] or Zn–Mn [11]. Citrate is also used in electrodeposition baths in which it is not expected to act as a complexing agent, such as solutions containing diverse cyanocomplexes. In this context, the usage seems rooted in the empirical industrial practice, which has been in successful operation since the 70s [12,13]. In spite of the relatively widespread use of  $\text{KAu}(\text{CN})_2$  citrate baths, the specific electrochemical effects of citrate have not been addressed explicitly. In addition, also Au(I) cyanocomplex baths containing citrates or phosphates as the electrolytes are sometimes incorporated in industrial practice [14] and it was shown that marked differences emerge in the workability of Au–Cu alloy electrodeposition systems from  $\text{KAu}(\text{CN})_2$  and Cu(II)–EDTA if phosphate is substituted for citrate [15].

We are not aware of any spectroelectrochemical studies on the Au–citrate system during electrodeposition having been published so far. The first electrochemical in situ FTIR study of citrate on Au(111) appeared during the write-up of this paper [16]. These authors provide in depth information on the citrate–Au system in an acidic aqueous solution on a static single-crystal electrode.

This work deals with the electrochemical behaviour of gold in citrate solution and under conditions of gold electrodeposition and oxidation from cyanoaurate baths, by means of cyclic voltammetry and in situ FTIR investigations. For this purpose, the behaviour in a close-to-neutral citrate solution of a polycrystalline gold electrode polarised in a potential range encompassing both cathodic and anodic conditions (in the presence of  $\text{CN}^-$ ,  $\text{KAu}(\text{CN})_2$  or  $\text{KAu}(\text{CN})_4$ ) is analysed.

In this paper, we highlight some relationships between the nature of the organic additive and the electrochemical behaviour of adsorbed cyanide deriving either from free  $\text{CN}^-$  present in the solution or pre-adsorbed at the electrode, or released by reduction of  $\text{Au}(\text{CN})_2^-$  or  $\text{Au}(\text{CN})_4^-$  during the electrodeposition of Au. Details of the surface species forming under cathodic and anodic polarisation in the presence of citrate are given. The formation of different kinds of Au– $\text{CN}^-$  films at the electrode has been recognised and the effects of citrate on their stability have been ascertained. Our investigation also spans the anodic range, since Au soluble anodes are commonly used in metal plating processes from cyanide baths. We are, therefore, interested in highlighting the behaviour of the gold–citrate–cyanide system also in the anodic regime in terms of citrate reactivity and Au oxidation reactions.

## 2. Experimental

Chemicals used were of analytical grade: citric acid tri-sodium salt dihydrate  $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3 \cdot 2\text{H}_2\text{O}$  (from Fluka, minimum assay 99%); sodium cyanide NaCN (from Fluka, minimum assay 97%); potassium dicyanoaurate  $\text{KAu}(\text{CN})_2$  and potassium tetracyanoaurate  $\text{KAu}(\text{CN})_4$  (from Engelhard). The solutions were prepared with ultrapure water of 18.2 M $\Omega$  cm resistivity from a Millipore-Milli-Q system. All experiments were carried out at room temperature. A gold polycrystalline electrode was employed as the working electrode (WE) and the reference electrode was a reversible hydrogen electrode (RHE) immersed in the test solution (0.3 M trisodium citrate solution) through a Luggin capillary. The potential scan rate for the cyclic voltammograms was 50 mV s $^{-1}$ . Five systems with a pH of 7 were investigated: (a) 0.3 M aqueous solution of trisodium citrate; (b) adsorption of a cyanide adlayer on the gold surface at open circuit potential and then transfer to a 0.3 M trisodium citrate solution; (c) a 0.3 M trisodium citrate + 0.1 mM NaCN aqueous solution; (d) a 0.3 M trisodium citrate + 0.1 M  $\text{KAu}(\text{CN})_2$  solution; and finally (e) a 0.3 M trisodium citrate + 0.1 M  $\text{KAu}(\text{CN})_4$  solution.

The in situ FTIR experiments were carried out with a Nicolet Magna 850 spectrometer equipped with a liquid nitrogen-cooled MCT detector. The three-electrode spectrochemical cell incorporated a prismatic  $\text{CaF}_2$  window bevelled at 60°. The spectral resolution employed was 8 cm $^{-1}$  and all the spectra are presented as  $\Delta R/R$ .

## 3. Results and discussion

### 3.1. Spectroelectrochemical behaviour of citrate at the Au surface

Fig. 1 shows the cyclic voltammogram recorded for a polycrystalline gold electrode immersed in a 0.3 M citrate test solution, for which, key features of the Au surface in this medium are easily recognised. On the one hand, both the gold surface oxidation and the electrolyte oxidation take place above 1.25 V. The oxide layer is reduced during the reverse scan through a broad cathodic peak at ca. 1.1 V. On the other hand, the appearance of a broad reversible, voltammetric peak centred at around 0.5 V seems to be compatible with the onset of citrate anion adsorption. A magnification of this voltammetric features is displayed in the inset of Fig. 1. It should be noted that the gold surface usually presents the charging of the double layer in this potential range. In addition, a voltammetric profile of this kind is very characteristic of the occurrence of reversible adsorption of anions on noble metal surfaces [17–19].

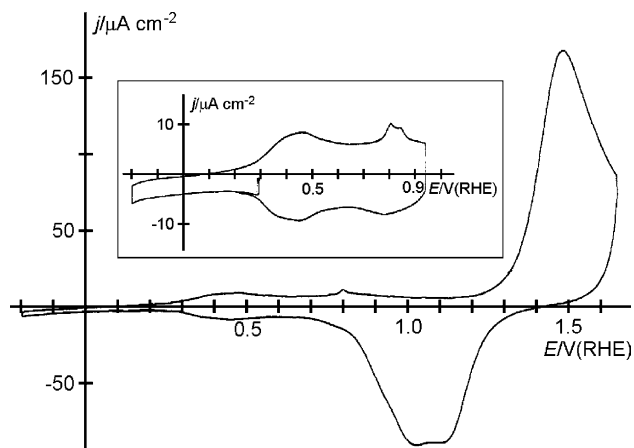


Fig. 1. Cyclic voltammograms recorded for a gold electrode in 0.3 M sodium citrate solution. Inset: magnification in the  $-0.2$  to  $1.0$  V potential range.

To confirm this point, the Au/citrate system was investigated by means of in situ FTIR spectroscopy and the results are shown in Fig. 2.

A flame-treated gold disk electrode was transferred to the spectroelectrochemical cell and immersed at  $0.1$  V in the  $0.3$  M citrate test solution. A set of 100 interferograms was collected at this potential to be used as the reference spectrum. The potential was then stepped in the positive direction from  $0.1$  up to  $1.4$  V and a sample spectrum was acquired for each step. Then, each of the sample spectra was referred to the spectrum collected previously at  $0.1$  V in such a way that the spectroscopic changes eventually induced by the potential at the Au–citrate solution interface can be easily monitored. The results are shown in Fig. 2(a), for which the evolution of

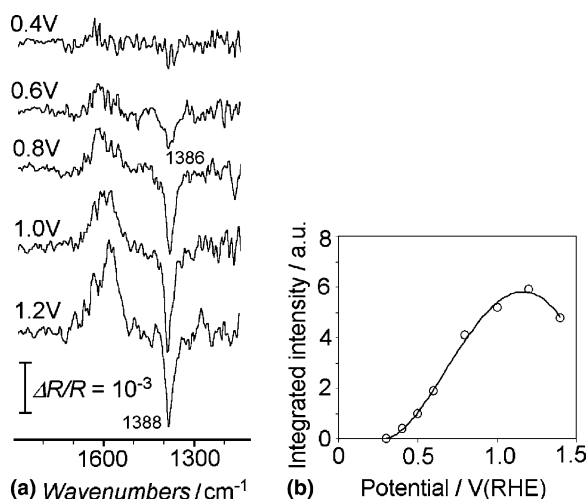


Fig. 2. (a) Set of in situ FTIR spectra collected at the sample potentials indicated for a gold electrode in  $0.3$  M sodium citrate medium. Reference potential  $0.1$  V. p-polarised radiation. 100 scans at each potential. (b) Potential dependence of the integrated band intensity for the absorption at  $1386$   $\text{cm}^{-1}$ . Data obtained from (a).

the in situ FTIR spectrum, as the sample potential is made more positive, can be followed from top to bottom in the spectral range comprised between  $1100$  and  $1900$   $\text{cm}^{-1}$ . The main observable feature at potentials ranging from  $0.4$  up to  $1.2$  V is the evolution of a negative-going absorption band at  $1386$   $\text{cm}^{-1}$  whose intensity increases continuously with the applied potential and whose peak centre shifts with a subtle tuning rate of about  $6$   $\text{cm}^{-1} \text{V}^{-1}$ . As this absorption was not detected when the experiment was reproduced with s-polarised radiation, the  $1386$   $\text{cm}^{-1}$  band should be attributed to the existence of a potential-induced adsorption of some species. The observed frequency lies in the spectral region characteristic of the symmetric O–C–O stretch of two-fold coordinated carboxylate anions [16–20] either in a bridge or on-top configuration. This finding seems fully compatible with both the chemical nature of the electrolyte employed and the voltammetric features displayed in Fig. 1 at ca.  $0.5$  V. In addition, from the in situ FTIR spectroscopic investigation of the Au(111)/citrate system carried out in [16] it was concluded that, in high pH electrolytes, citrate adsorbs through the carboxylate in a  $\eta$ -2 bonded structure. Possible bonding configurations of this adsorbate were also discussed, based on one, two or all three carboxylate groups coordinating to the Au(111) surface. The surface coverage of an adsorbed species is generally related to the intensity of the IR absorption band. Thus, for the particular system under investigation, the coverage of citrate anions can be related to the intensity of the feature at ca.  $1386$   $\text{cm}^{-1}$  in Fig. 2(a). The integration of this absorption band can be used to monitor the change in the population of adsorbed molecules, as the potential is made more positive. Then, as deduced from Fig. 2(b), the maximum coverage of surface citrate is obtained at around  $1.2$  V, prior to the onset of citrate oxidation. When the potential increases up to  $1.4$  V, a positive band at  $2345$   $\text{cm}^{-1}$  is observed in the spectrum which can be assigned to dissolved  $\text{CO}_2$ . This result indicates the oxidation of citrate anion at this potential. Then, from the results presented, it can be deduced that: (i) citrate anions adsorb through a carboxylate group to the gold surface at potentials higher than  $0.4$  V; (ii) the surface coverage of citrate increases with the applied potential, reaching a maximum at around  $1.2$  V; and (iii) citrate anions are oxidized beyond  $1.2$  V.

### 3.2. Cyanide adsorption and oxidation at the Au surface in citrate medium

As a previous step in the investigation of the electrochemical reactivity of gold cyanocomplexes in citrate medium, we will characterize here the behaviour of those cyanide adlayers formed ex situ during the open circuit contact between a gold electrode and a dilute  $\text{CN}^-$  solution and, additionally, also the behaviour of

bulk cyanide at the Au electrode in the citrate electrolyte. Fig. 3 shows the cyclic voltammogram recorded for a gold electrode, which was covered with a cyanide adlayer and subsequently immersed in the citrate test solution. The presence of adsorbed cyanide results in several voltammetric modifications when this curve is compared with the profile obtained for the bare Au surface in the same electrolyte (Fig. 1). On the one hand, the anodic peak related to the formation of the gold surface oxide and electrolyte oxidation is shifted by 80 mV in the positive direction. In addition, the broad reversible peak pointing to the onset of citrate adsorption seems to be shifted at least to 0.9 V, as can be observed better in the inset of Fig. 3. In order to obtain vibrational information from the Au-CN<sub>ads</sub> system, a gold electrode covered with cyanide was transferred to the spectrochemical cell and the spectra of Fig. 4 were recorded. Sample potentials are those indicated for each spectrum, whereas the reference was collected at 1.6 V after the entire sample series was acquired. This working method allows us to present the absorption band of adsorbed cyanide at around 2100 cm<sup>-1</sup> with monopolar character because CN<sub>ads</sub> has oxidized completely at 1.6 V. The potential dependence of both peak frequency and integrated intensity of the cyanide band can thus be obtained from the spectra of Fig. 4. Both potential dependences are represented in the plot of Fig. 5, from which it is derived that the Stark shift of the C-N stretching band is 23 cm<sup>-1</sup> V<sup>-1</sup>. Fig. 5 also reveals the continuous decrease in the intensity of the cyanide absorption band, which can be attributed to the decrease in the surface coverage of cyanide, either as a consequence of its oxidation or to dissolution via the formation of gold cyanocomplexes [21,22]. As the appearance of dissolved carbon dioxide cannot be perceived until potentials of 1.4 V are reached, those CO<sub>2</sub> molecules are

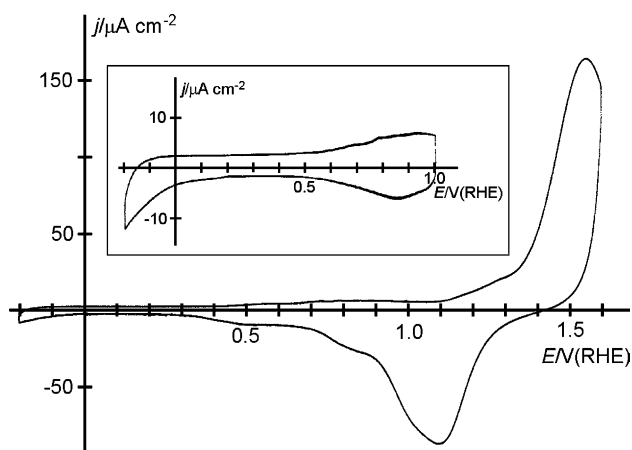


Fig. 3. Cyclic voltammograms recorded for a gold electrode surface pre-covered with a cyanide adlayer and then immersed in a 0.3 M sodium citrate solution. Inset: magnification of the -0.2 to 1.0 V potential range.

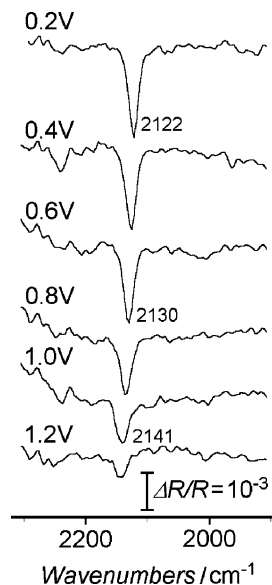


Fig. 4. In situ FTIR spectra for a gold electrode covered with cyanide in 0.3 M sodium citrate solution. Reference potential 1.6 V. Sample potentials indicated. p-polarised radiation. 100 scans at each potential.

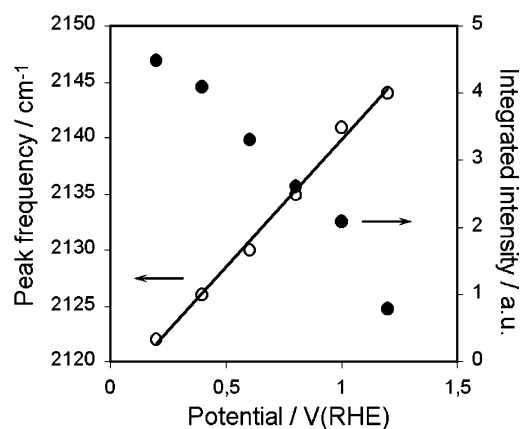


Fig. 5. Potential dependence of the peak frequency (solid circles) and the integrated band intensity (open circles) for the C-N stretching of adsorbed cyanide. Data obtained from Fig. 4.

believed to come from the oxidation of citrate rather than from the oxidation of CN<sub>ads</sub>. Further evidence pointing to the formation of gold cyanocomplexes from the Au-CN system in citrate medium can be obtained when cyanide ions are present in the electrolyte solution at very low concentration. Fig. 6(a) shows the in situ FTIR spectrum collected at 1.4 V and referred to that obtained at 0.4 V for a gold disk electrode immersed in a 0.3 M citrate + 0.1 mM cyanide working solution. Under these conditions, what appears to be a bipolar absorption band is seen in the frequency range of the C-N stretching for adsorbed or co-ordinated cyanide. In addition, Fig. 6(b) shows an in situ FTIR spectrum obtained between the same potential limits for a gold surface previously covered with cyanide and then im-

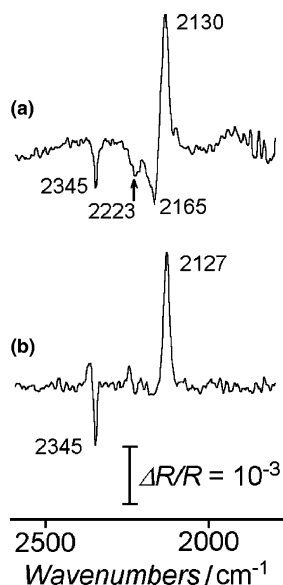


Fig. 6. In situ FTIR spectra collected for: (a) a bare Au electrode immersed in a 0.3 M sodium citrate + 0.1 mM sodium cyanide solution; (b) Au electrode previously covered with a cyanide adlayer immersed in a 0.3 M sodium citrate solution free of bulk cyanide. Sample potentials 1.4 V. Reference potentials 0.4 V. 100 interferograms were collected at each potential.

mersed in a working solution free of bulk cyanide. The C–N stretching appears here with positive character indicating the removal of adsorbed cyanide at 1.4 V. By comparing both spectra, it can be concluded that the negative-going band observed at 2165  $\text{cm}^{-1}$  in the spectrum (a) is not a manifestation of the Stark effect, but points to the formation of a distinct species at the sample potential. As this frequency fits well with the C–N stretching of the gold (I) cyanocomplex  $\text{Au}(\text{CN})_2^-$ , 2164  $\text{cm}^{-1}$  [20], the oxidation and dissolution of the electrode surface via the generation of this co-ordination compound seems proved. Coupled with the formation of the  $\text{Au}(\text{CN})_2^-$  complex, the oxidation of bulk cyanide at such high potential values yields small amounts of soluble cyanate ions, as testified by the small absorption band at 2223  $\text{cm}^{-1}$  observed in the spectrum (a). Finally, it is worth mentioning another interesting feature related to the  $\text{Au}-\text{CN}_{\text{ads}}$  system, such as the confirmation that citrate adsorption is fully inhibited when adsorbed cyanide is fully covered. Thus, the onset of citrate adsorption on the gold electrode covered with cyanide can be detected by in situ FTIR spectroscopy only when the  $\text{CN}_{\text{ads}}$  coverage has decreased significantly, namely at potentials as positive as 1.0 V. This value represents a 600 mV shift to positive in relation to the Au/citrate system described in Figs. 1 and 2. In this context, the absorption bands observed at 2345  $\text{cm}^{-1}$  in the two spectra of Fig. 6 are due to the generation of dissolved  $\text{CO}_2$  coming from the oxidation of citrate at the sample potential.

### 3.3. Spectroelectrochemical behaviour of $\text{Au}(\text{CN})_2^-$ complexes in citrate medium

Once the behaviour of citrate and cyanide has been analysed, we will refer to the voltammetric and spectroscopic response of either Au(I) or Au(III) cyanocomplexes at the gold surface. Cyclic voltammograms recorded in citrate solution containing 0.1 M  $\text{Au}(\text{CN})_2^-$  are presented in Fig. 7. The steady voltammogram shown in the main figure differs from that obtained in the absence of  $\text{Au}(\text{CN})_2^-$  in the test solution. During the forward scan a small voltammetric peak appears at 1.1 V, which is followed by an intense anodic peak at around 2 V. For the reverse scan, a broad cathodic peak appears at around 1 V, corresponding to the reduction of the surface oxide layer formed during the positive scan. The sharp anodic peak at 2 V can be assigned to the joint oxidation of citrate, Au(I) cyanocomplex and gold electrode surface. From the comparison of this voltammetric profile with that obtained in the absence of Au(I) cyanocomplex, it is inferred that the oxidation processes of citrate and gold surface are shifted to higher potential values. This shift is even higher than that obtained in a working solution containing free cyanide ions (voltammogram not shown). At more negative potentials a cathodic peak is observed at  $-0.1$  V that corresponds to the gold deposition from the  $\text{Au}(\text{CN})_2^-$ . If the scanning potential limits are restricted between 0.2 and 1.3 V, the small peak at 1.1 V shows a reversible counterpart at 0.85 V during the reverse scan with a measured charge close to 80  $\mu\text{C cm}^{-2}$  (see inset of

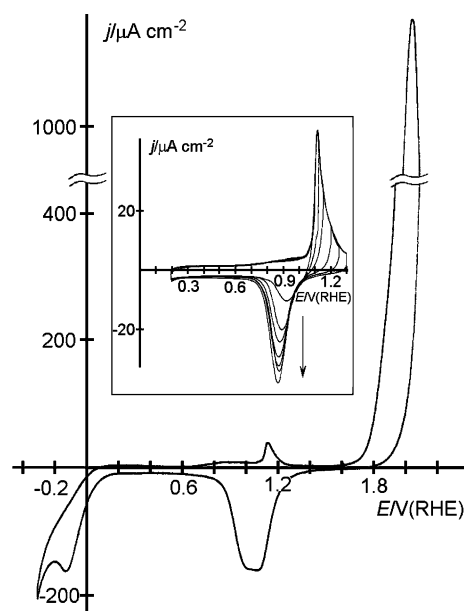


Fig. 7. Cyclic voltammograms recorded for a gold electrode in a 0.3 M sodium citrate + 0.1 M  $\text{KAu}(\text{CN})_2$  solution. Inset: effect of increasing the upper potential limit on the voltammetric charge of the cathodic peak at 0.9 V.

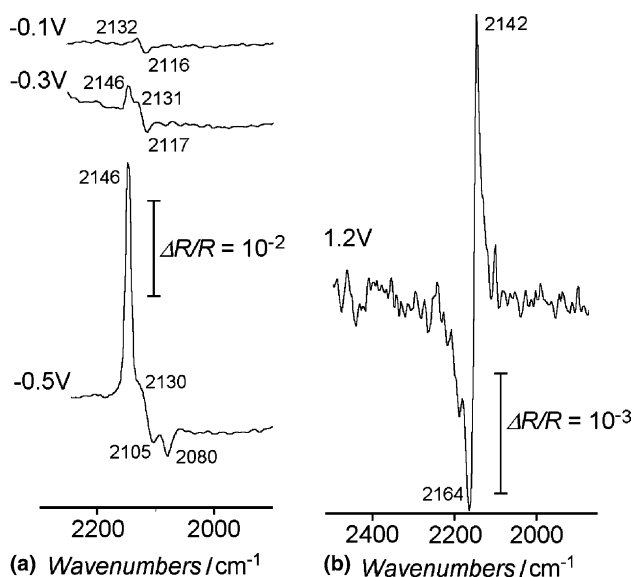


Fig. 8. In situ FTIR spectra for a gold electrode in 0.3 M sodium citrate + 0.1 M  $\text{KAu}(\text{CN})_2$  solution at the sample potentials indicated in each spectrum. Reference potential: (a) 0.0 V; (b) 0.7 V. (a) 100 and (b) 500 interferograms were collected for each spectrum.

Fig. 7). Upon stirring, most of the voltammetric charge associated with the pair of peaks is still recorded. As deduced from this result, the species that gives rise to the pair of peaks should be attached to the electrode surface. It is very difficult to ascertain the true nature of the surface process responsible for the appearance of this voltammetric feature, mainly because, as will be seen below, the in situ FTIR experiments performed did not shed much light on the problem. In spite of this, it is worth mentioning that Sawaguchi et al. [23] studied the formation of aurous cyanide ( $\text{AuCN}$ ) adlayers on Au(111) surfaces from neutral solutions containing  $\text{KAu}(\text{CN})_2$  by STM, LEED and CV techniques. They found that the  $(\text{AuCN})_{\text{ads}}$  formed from the Au(I) cyanocomplex exists at potentials as positive as 0.8 V more positive than the potential for the bulk deposition of gold. Besides, the so-called surface film of aurous cyanide seemed to undergo a surface transformation that gave rise to the appearance of a pair of reversible voltammetric peaks. Regardless of the fact that the  $\Delta E_p$  for the polycrystalline substrate is much higher than for the

Au(111) surface, a transformation of the surface film (manifested either as a phase transition or as an electrochemical transformation) undergone by a AuCN adlayer in citrate medium could be at the origin of the voltammetric peaks observed in the inset of Fig. 7 for the polycrystalline substrate.

The voltammetric response of the Au(I) cyanocomplex can be compared with its spectroscopic behaviour. Thus, Fig. 8 shows in situ FTIR spectra obtained for a gold polycrystalline surface immersed in a 0.3 M sodium citrate + 0.1 M  $\text{KAu}(\text{CN})_2$  solution. Sample potentials are those indicated for each spectrum, whereas the reference potential was collected at 0.0 V for Fig. 8(a) and at 0.7 V for Fig. 8(b). The spectra collected when the sample potential is scanned from  $-0.1$  down to  $-0.5$  V are shown in Fig. 8(a). A bipolar band centred at  $2124 \text{ cm}^{-1}$  appears in the spectra recorded at  $-0.1$  V which corresponds to the C–N stretching of adsorbed cyanide, its bipolar character being a manifestation of the Stark effect, which shifts the absorption to blue at higher potentials. When the applied potential reaches  $-0.3$  V, a new positive-going band develops at  $2146 \text{ cm}^{-1}$  with partial overlapping of the bipolar band at around  $2124 \text{ cm}^{-1}$ . The intensity of the new absorption band rises when the potential reaches a value of  $-0.5$  V and, at the same time, a new negative band appears at  $2080 \text{ cm}^{-1}$ . The positive-going band at  $2146 \text{ cm}^{-1}$  can be easily assigned to the depletion of Au(I) cyanocomplex from the solution due to its consumption upon gold deposition at the negative potentials involved (Table 1). This assignment is in agreement with the observation of this band when s-polarised light is employed. Finally, the feature at  $2080 \text{ cm}^{-1}$  corresponds to the free cyanide ion in solution which is released from  $\text{Au}(\text{CN})_2^-$  as a consequence of the rupture of the gold cyanocomplex. In order to obtain spectroscopic information from the redox couple observed in the inset of Fig. 7, an in situ FTIR spectrum collected between 1.2 (sample) and 0.7 V (reference) was obtained in this solution and is presented in Fig. 8(b). This potential interval corresponds to the reversible peaks observed in the voltammogram. The main feature observed in the spectrum is a bipolar band centred at  $2153 \text{ cm}^{-1}$  that was not detected when the experiment was reproduced with s-polarised

Table 1  
In situ FTIR bands and their proposed assignments

Vibrational mode	Assignment	Frequency/ $\text{cm}^{-1}$	References
O–C–O symmetric stretch	(citrate) $_{\text{ads}}$	1386	[16–20]
C–N stretch	Free $\text{CN}^-$	2080	[24]
C–N stretch	$(\text{CN})_{\text{ads}}$	2120–2140	[17,25]
C–N stretch	Free $\text{Au}(\text{CN})_2^-$	2146	[20]
C–N stretch	$\text{AuCN}$	2153	[20]
C–N stretch	Free $\text{Au}(\text{CN})_2^-$	2164	[20]
O–C–N asymmetric stretch	Free $\text{OCN}^-$	2223	[24]

radiation. This fact provides clear evidence pointing to the fact that the species responsible for the pair of voltammetric peaks is present on the electrode surface. As the frequency of  $2153\text{ cm}^{-1}$  is also compatible with the C–N stretching of metal cyanide complexes [20], the bipolar feature can be interpreted as an effect of the electrode potential (Stark effect) on the C–N bond in the AuCN film deposited on the gold electrode although no information on the nature of the surface process can be obtained.

Now we will focus on the electrochemical behaviour of the  $\text{Au}(\text{CN})_4^-$  complex. Fig. 9 shows the steady voltammogram of a gold polycrystalline electrode immersed in a 0.3 M sodium citrate + 0.1 M  $\text{KAu}(\text{CN})_4$  solution. During the forward scan, an anodic peak appears centred at around 1.6 V. This feature is related to two distinct processes: the oxidation of the gold electrode surface and the oxidation of the citrate electrolyte. Additionally, the reverse scan shows two overlapped cathodic peaks at around 1 V which can be associated with the reduction of the gold oxide adlayers formed during the positive scan. At more negative potentials, a voltammetric peak appears at  $-0.1\text{ V}$  corresponding to the deposition of gold from the Au(III) cyanocomplex. As in the case of the voltammogram recorded in the presence of  $\text{Au}(\text{CN})_2^-$  (Fig. 7), the formation of the gold surface oxide is shifted to higher potential values when compared with the voltammogram obtained in a solution free of cyanocomplex. However, the shift here is lower than in that case.

Fig. 10 shows the in situ FTIR spectra obtained for a gold polycrystalline surface in a 0.3 M sodium citrate + 0.1 M  $\text{KAu}(\text{CN})_4$  solution. Sample potentials are indicated in the figure and the reference potential was collected previously at 0 V. Fig. 10(a) shows the spectra collected in a potential excursion from  $-0.1$  down to  $-0.5$

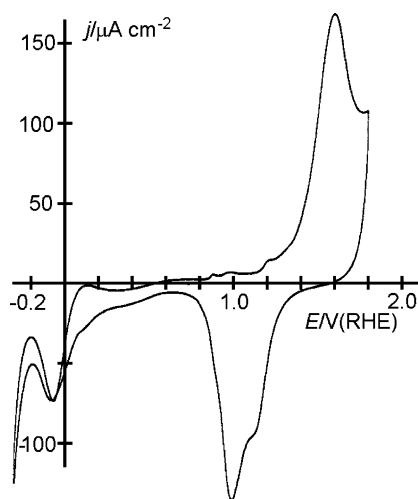


Fig. 9. Cyclic voltammogram recorded for a gold electrode in a 0.3 M sodium citrate + 0.1 M  $\text{KAu}(\text{CN})_4$  solution.

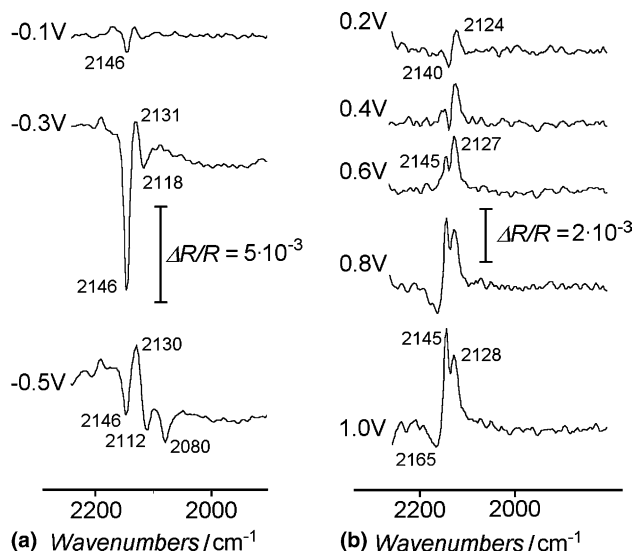


Fig. 10. In situ FTIR spectra for a gold electrode in 0.3 M sodium citrate + 0.1 M  $\text{KAu}(\text{CN})_4$  solution at the sample potentials indicated in each spectrum. Reference potential 0.0 V. 100 interferograms collected for each spectrum.

V, in an experiment similar to that performed for Fig. 8(a). The spectrum collected at  $-0.1\text{ V}$  shows a negative-going band at  $2146\text{ cm}^{-1}$ , which is also present when the experiment is reproduced with s-polarised radiation. This fact indicates that the absorption is due to a species currently in solution. The intensity of the band increases as the potential is lowered down to  $-0.3$  and  $-0.5\text{ V}$ . On the other hand, a positive-going band peaking at ca.  $2130\text{ cm}^{-1}$  is also observed in all the spectra of Fig. 10(a). At  $-0.3\text{ V}$ , the monopolar character of this band changes to bipolar, the feature being centred at  $2125\text{ cm}^{-1}$ . The bipolar band cannot be detected when s-polarised light is employed, so it should be assigned to the C–N stretching of an adsorbed species, such as adsorbed cyanide. At  $-0.5\text{ V}$  a negative band develops at  $2080\text{ cm}^{-1}$ , which is also observed with s-polarised radiation. This feature is thus assigned to the presence of cyanide ions in the working solution. With regard to the feature at  $2146\text{ cm}^{-1}$ , the characteristic frequency makes it possible to associate the band with the formation of  $\text{Au}(\text{CN})_2^-$  from the reduction of  $\text{Au}(\text{CN})_4^-$  at increasing negative potentials. This Au(I) cyanocomplex is finally reduced during the gold deposition and free cyanide is released into the working solution. Finally, Fig. 10(b) shows the in situ FTIR spectra obtained in a potential excursion made in the positive direction from 0 V. At  $0.2\text{ V}$  the spectrum shows a bipolar band centred at  $2132\text{ cm}^{-1}$  that can be assigned to adsorbed cyanide. This bipolar band seems to be still visible in all the spectra of the series but from  $0.6\text{ V}$  an overlapping band develops at around  $2145\text{ cm}^{-1}$ . Both features can be associated with the disappearance of adsorbed cyanide and Au(III) cyanocomplex, respectively, at increasing positive potentials. The hypothesis is sup-

ported by the fact that the intensities of both bands rise as the potential is made more positive. The negative-going band at  $2165\text{ cm}^{-1}$  which is clearly observed at 1.0 V could correspond to the formation of gold cyanate complexes from the oxidation of the  $\text{Au}(\text{CN})_4^-$ .

#### 4. Conclusions

From the results presented in this work, it has been deduced that: (i) citrate anions adsorb through carboxylate groups to the gold surface at potentials higher than 0.4 V; and (ii) the surface coverage of citrate increases with the applied potential, citrate being oxidized beyond 1.2 V. The adsorption of citrate on a gold surface covered by cyanide can take place only when most of the adsorbed cyanide is desorbed from the electrode surface.

The voltammogram recorded in a citrate solution in the presence of  $\text{KAu}(\text{CN})_2$  shows a reversible couple that inhibits the subsequent oxidation of both the gold surface and citrate anions. Based on reported results, this reversible couple has been assigned tentatively to the formation of an AuCN film on the electrode surface. On the contrary, the film seems not to be formed in a citrate solution that contains the  $\text{KAu}(\text{CN})_4$  complex. The electrochemical reduction of this latter cyanocomplex yields  $\text{Au}(\text{CN})_2^-$  as a prior step to the gold deposition. The generation of an adsorbed cyanide adlayer has been detected during the electrodeposition of gold from these cyanocomplexes. This adsorbed cyanide can be finally oxidized to cyanate at higher potentials.

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