Electrochemistry Communications 74 (2017) 1–4

Contents lists available at ScienceDirect

Electrochemistry Communications

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

Formation of cyanuric acid from cyanate adsorbed at gold electrodes

William Cheuquepán [b], Antonio Rodes [a,b], José M. Orts [a,b,*], Juan M. Feliu [a,b]

[a] Departamento de Química Física, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain
[b] Instituto Universitario de Electroquímica, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain

ARTICLE INFO

Article history:
Received 31 October 2016
Received in revised form 8 November 2016
Accepted 8 November 2016
Available online 12 November 2016

Keywords:
ATR-SEIRAS
Cyanate
Cyanuric acid
Cyanurate
DFT
Au(111)

ABSTRACT

We report the formation of cyanuric acid species at Au(111) electrodes in cyanate-containing solutions, due to the electroless trimerization of isocyanic acid. Similar experimental bands in the range between 1300 and 1900 cm^{-1} are observed in Surface Enhanced Infrared Reflection Spectroscopy experiments under Attenuated Total Reflection conditions (ATR-SEIRAS) with solutions containing either cyanate anions at high concentration or cyanuric acid. The experimental frequencies agree well with those obtained from Density Functional Theory (DFT) calculations for the adsorbed cyanurate anion, bonded to the metal in a tridentate configuration, with its molecular plane perpendicular to the metal surface.

1. Introduction

We have previously reported [1] a study of the adsorption of cyanate anions at Au(111) and Au(100) single crystal electrodes, combining external reflection spectroelectrochemical experiments and Density Functional Density (DFT) calculations. Taking into account the calculated optimized adsorbate geometries, adsorption energies and vibrational harmonic frequencies, we assigned the adsorbate bands found experimentally between 2100 and 2300 cm^{-1}. In agreement with previous works [2–5], these bands correspond to the asymmetric OCN stretch of N-bonded, specifically adsorbed isocyanate anions, mainly occupying on-top sites, with their molecular axis preferentially oriented in the direction perpendicular to the metal surfaces.

In this paper we report new spectral features observed experimentally using in situ Surface Enhanced Infrared Reflection Spectroscopy under Attenuated Total Reflection conditions (ATR-SEIRAS) and Au(111)-25 nm thin-layer electrodes. The ATR-SEIRAS technique [6–7] is especially advantageous for studying interfacial species, because of the strong exaltation of the infrared absorption by adsorbates and double-layer solvent molecules. An additional advantage is the removal of interferences due to the bulk solvent. Both advantages help in the observation of new absorption bands not detected in the external reflection experiments [1–5], that suggest the formation of new adsorbed chemical species. We show in this report that the observed bands are characteristic of species derived from cyanuric acid ($C_3N_3O_3H_3$), a very stable cyclic trimer of isocyanic acid (HNCO). Cyanuric acid [8] can be synthesized by thermal condensation of three urea molecules, with simultaneous release of three ammonia molecules, or starting from metal cyanates in alkaline solutions. Cyanuric acid behaves as a weak acid. From its pKa values (6.88, 11.40, 13.5) [9] the only species that are expected to exist in significant amounts both in solution and at the electrified interface are the undissociated acid and the cyanurate monoanion ($C_3N_3O_3H_2^-$), that results from the first acid dissociation equilibrium. In this anion the negative charge on the N atom is stabilized by the two neighbouring carbonyl groups.

In order to support this interpretation, we have compared the voltammetric behaviour and the ATR-SEIRA spectra obtained with solutions containing either cyanate salts or cyanuric acid. We have also carried out periodic DFT calculations of geometry and frequencies for the cyanurate anion adsorbed at the electrode surface. These calculations will provide the basis for the assignment of the experimental vibrational bands.

2. Experimental and computational details

Working solutions were obtained by dissolving either sodium cyanate (96%, Sigma-Aldrich) or cyanuric acid (98%, Sigma-Aldrich), in a solution of sodium perchlorate (99.99%, Sigma-Aldrich) prepared in ultrapure water (18.2 MΩ cm, Elga-Vivendi). These solutions were deaerated with Ar (N50, Air Liquide) and blanketed with this gas during the experiments. Solutions in deuterated water were prepared with deuterium oxide (99.9 at.%D, Aldrich) which was used as received. In all the spectroelectrochemical experiments a Ag/AgCl/KCl (sat) electrode and a gold wire were used as the reference and the counter electrode, respectively. Details for the ATR-SEIRAS experiments regarding

---

[*] Corresponding author at: Departamento de Química Física, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain.
E-mail address: jm.orts@ua.es (J.M. Orts).

http://dx.doi.org/10.1016/j.elecom.2016.11.005
1388-2481/

both the preparation of the gold thin film electrodes and the collection of the in situ infrared spectra can be found in previous works [10,11].

Projector-augmented-wave [12–13] DFT calculations of the cyanurate anion adsorbed on a model Au(111) surface were carried out using the VASP [14–17] code (version 4.6), with the PBE [18–19] functional.

The slab used for modeling a (3 × 3) cell of the Au(111) surface consisted of 4 metallic layers (with 9 Au atoms per layer). The structure of one adsorbed cyanurate species was optimized while the positions of the metal atoms were kept fixed at their bulk equilibrium distances (0.29520 nm) calculated with the same functional. A vacuum region (of more than 12 Å) was used for separating the slabs in the Z direction.

Sampling of the Brillouin zone used a Monkhorst-Pack [20] (3 × 3 × 1) scheme and for smearing we used the Methfessel-Paxton [21] method (second order, sigma = 0.2 eV). The convergence criteria used were: 10^{-5} eV for electronic convergence, and 0.02 eV/Å for the forces.

3. Experimental results

Curve b in Fig. 1 shows the cyclic voltammogram obtained with a gold thin film electrode with preferential (111) orientation (denoted Au(111)-25 nm in the following [7]) in contact with a 10 mM NaOCN + 0.08 M $NaClO_4$ solution. As previously reported for Au(111) and Au(100) electrodes [1], a significant charge contribution associated with the presence of cyanate is superimposed on the voltammetric response of the cyanate-free solution (curve a) for potentials above −0.20 V. No significant faradic oxidation currents that could be related to the irreversible oxidation of cyanate anions can be detected in the explored potential region. A broad feature centered at 0.25 V and a peak at ca. 0.35 V are observed in the positive going sweep for the 10 mM solution.

Fig. 2 shows a series of potential-dependent ATR-SEIRA spectra collected for the Au(111)-25 nm electrode in contact with 10 mM NaOCN + 0.08 M $NaClO_4$ solutions prepared in water (A) or deuterium oxide (B). Spectra are referred to that collected in the same solution at −0.5 V. A potential-dependent feature is observed for adsorbed cyanate at 2150–2230 cm^{-1}[1–5]. In addition, several positive-going features appear between 1800 and 1300 cm^{-1}. First, a clearcut feature appears at ca. 1716 cm^{-1} in the spectrum collected at −0.40 V, being blueshifted up to 1743 cm^{-1}at 0.60 V. This feature is accompanied by a shoulder at ca. 1781 cm^{-1}. Moreover, additional features are observed at 1654, 1496, 1388 and 1330 cm^{-1}. The intensities of all these features increase with the electrode potential up to 0.60 V and decrease down to zero when the electrode potential is stepped back to −0.50 V (not shown). In order to avoid interferences from the bending modes of interfacial water, additional experiments were carried out in deuterium oxide. Potential-dependent absorption bands are also clearly observed. Positive-going features appear (panel B in Fig. 2) at ca. 2213, 1789,1720, 1650, 1581, 1480 and 1438 cm^{-1} (all these frequency values measured in the spectrum collected at 0.60 V), some of them showing a band frequency strongly dependent on the electrode potential.

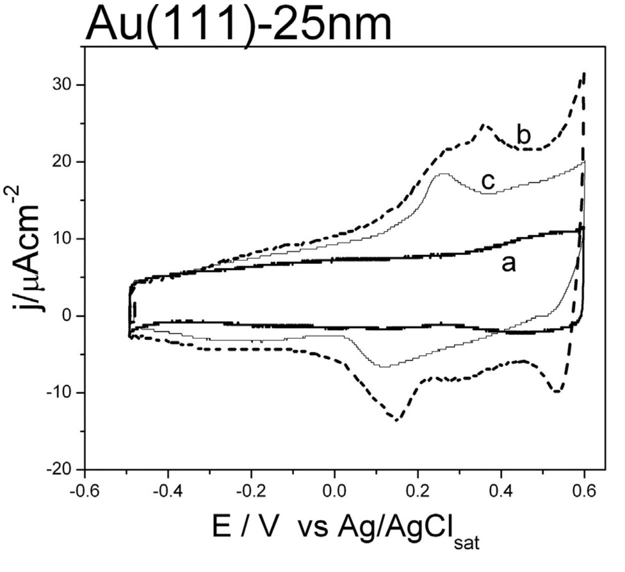

Fig. 1. Stationary cyclic voltammograms of a Au(111)-25 nm thin-layer electrode in contact with 0.08 M $NaClO_4$ solutions. a) Blank electrolyte; b) with added 10 mM NaOCN, and c) with added 0.1 mM cyanuric acid.

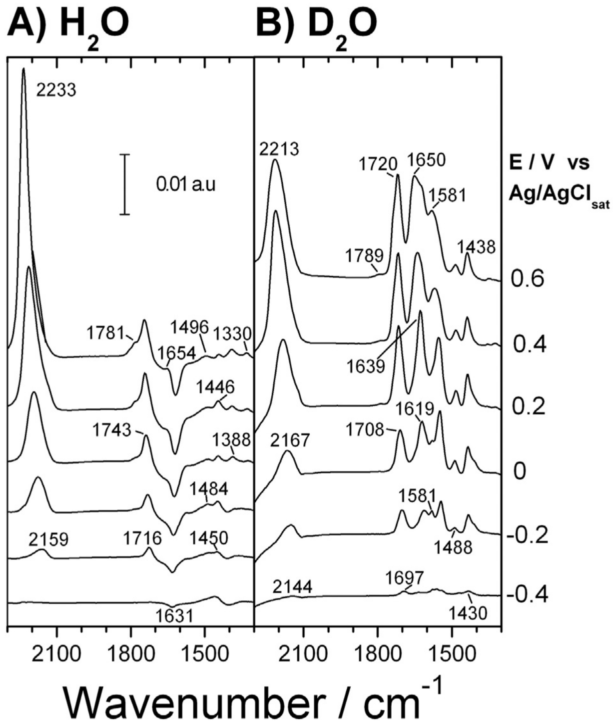

Fig. 2. Series of ATR-SEIRA spectra collected with a Au(111)-25 nm thin-layer electrode in contact with 0.08 M $NaClO_4$ + 10 mM NaOCN solutions in: A)H_2O; and B) D_2O. 100 interferograms were co-added with a resolution of 8 cm^{-1} at the indicated potentials and referred to the single beam spectrum collected at −0.50 V.

Except for the band at ca. 2213 cm^{-1}, none of the positive-going features observed between 1850 and 1300 cm^{-1} can be attributed to vibrational modes of adsorbed cyanate, pointing to the formation of other adsorbates. A relevant observation is that the most intense features appear in the spectral region for carbonyl groups [22]. This suggests the possibility of the trimerization of adsorbed cyanate, via its equilibrium with isocyanic acid, to form cyanuric acid or cyanurate as the final product.

$$3NCO^- \ (ads) + 3H^+ \leftrightarrows 3HNCO \ (ads) \rightarrow H_3C_3N_3O_3 \ (ads) \qquad (1)$$

Since this is a highly stable compound [8], spectroelectrochemical experiments in 0.08 M $NaClO_4$ solutions containing various concentrations of cyanuric acid were carried out. In this way, curve c in Fig. 1 corresponds to the voltammogram recorded in a 0.1 mM cyanuric acid-containing solution. Again, the voltammogram shows an excess of charge density with respect to the blank solution, attributable to reversible specific anion adsorption-desorption processes. Remark that the main feature in the cyanuric acid-containing solution appears at ca. 0.25 V and fits with the shoulder observed in the cyanate-containing solution.

ATR-SEIRAS experiments have been carried out in cyanuric acid-containing solutions with the Au(111)-25 nm electrode. In this work we limit our discussion to the spectra collected during a potentiostatic