



Effect of tetrabutylammonium cations on lifting of reconstruction and phase transitions within adsorbed adlayers at Au(100) electrode in halide electrolytes



Piotr Skořuda

Zakład Chemii Fizycznej, Wydział Chemii, Uniwersytet im. A. Mickiewicza, ul. Umultowska 89b, 61-614 Poznań, Poland

ARTICLE INFO

Article history:

Received 16 September 2015
 Received in revised form 22 November 2015
 Accepted 23 November 2015
 Available online 26 November 2015

Keywords:

Tetrabutylammonium cations
 Single-crystal Au(100) electrode
 Surface reconstruction
 Phase transitions within adsorbed adlayers

ABSTRACT

The influence of tetrabutylammonium (TBA) cations on lifting of reconstruction and phase transitions within adsorbed adlayers at Au(100) electrode in halide electrolytes has been studied by cyclic voltammetry and differential capacity measurements. The presence of TBA cation increases the stability range of the reconstructed surface more in chloride electrolyte than in bromide one in contrast to I^- anions which have no impact on stability range. Besides, TBA cations shift the spikes corresponding to the incommensurate structures of Br^- and Cl^- anion adlayers to less positive potentials and the spike assigned to the commensurate structure of Br^- anions in the opposite direction. In iodide electrolyte the two spikes connected most likely with the formation of the ordered cation/anion adlayers occur at less negative potential than the corresponding ones in TBA free solution.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Investigation of the specific adsorption of tetraalkylammonium cations started at the mercury/electrolyte interface (see Ref. [1] and references cited therein) and then has been extended to solid electrodes such as polycrystalline Au [2], Bi or Cd single crystal electrodes [3,4]. The latter studies were performed in aprotic media in order to establish the role of surface structure in processes occurring in non-aqueous supercapacitors [5]. Incidentally, tetraalkylammonium salts are commonly employed electrolytes in non-aqueous electrochemistry not only because of their good solubility in most organic solvents but also their low negative reduction potentials [6]. These compounds served also as components in the synthesis of the ionic liquids which have been applied in the copper electrodeposition [7].

Recently, we have done some preliminary work [8] on the adsorption of TBA cations on Au(100) and Au(111) electrodes, which was found to be structure sensitive and resemble those of simple organic molecules rather than those of ions. Moreover it has been suggested that adsorption of perchlorate anions from the supporting electrolyte lifts the reconstruction, which is modified by TBA cations on the surface.

However, as follows from literature [9], the replacement of perchlorate by halides *i.e.* anions of much stronger adsorbability, opens a new possibility to investigate the formation of close-packed ordered adlayer structures at single crystal electrodes. Thus to pursue the investigation it seems interesting to check the effect of TBA cations on the lifting of

reconstruction and the formation of ordered adlayer structures in halide electrolytes. To achieve this goal, in the present work, the interfacial properties of TBA cations at Au(100)/electrolyte interface were investigated in three supporting electrolytes KCl, KBr, and KI. We chose Au(100) single-crystal electrode as its surface reconstruction, from the (1×1) bulk termination structure to a rotated hexagonal (hex) one, and the presence of commensurate and incommensurate anion adlayer structures in halides, have been already well documented by studies ranging from electrochemical [10,11], scanning tunnelling microscopy (STM) [11–13] and surface X-ray scattering (SXS) [14,15] measurements to theoretical considerations [16,17]. One of the reasons for such widespread interest in these phenomena is their marked impact on some electrochemical processes *e.g.* phase transition in organic adlayer [18,19] or oxygen reduction reaction [20], respectively. In the following we use cyclic voltammetry as the above phenomena are nicely manifested by the occurrence of such voltammetric features as peaks and spikes, respectively.

These studies have shown that many aspects of the interfacial behaviour of TBA cations at Au(100) are influenced by the nature of the supporting electrolyte anions. Especially, the behaviour in KI differs from that in KCl or KBr.

2. Experimental

The working electrode was an Au(100) single crystal disc, 4 mm in diameter and 4 mm thick, and oriented to $<1^\circ$ (MaTeck, Jülich). Before each experiment the electrodes were prepared according to the well-known procedure for preparation of well-ordered gold surfaces [21].

E-mail address: pskoluda@main.amu.edu.pl.

Namely, the crystals were annealed for 3 min in a Bunsen burner flame, then cooled down to room temperature in a stream of nitrogen. Contact with the electrolyte was achieved by the hanging-meniscus method [22]. The counter electrode was an Au sheet. The reference electrode was a saturated calomel electrode (SCE) and throughout this work all potentials are reported *versus* SCE. The voltammetric measurements were recorded using an AUTOLAB system (Eco Chemie). All the voltammograms were obtained at a scan rate of 50 mV s^{-1} . In capacity measurements the potential was stepped in 10 mV divisions with a voltage of 6 mV amplitude and a frequency of 19 Hz.

The measurements were performed from solution of mixed electrolytes *i.e.* $5 \cdot 10^{-2} \text{ M}$ of supporting electrolyte + $5 \cdot 10^{-4} \text{ M}$ tetrabutylammonium perchlorate (TBAP). The choice of such a low concentration of TBAP is a consequence of its small solubility in water. The supporting electrolyte solutions were $5 \cdot 10^{-2} \text{ M}$ KCl, $5 \cdot 10^{-2} \text{ M}$ KBr and $5 \cdot 10^{-2} \text{ M}$ KI prepared from 99.99% salts from Sigma-Aldrich. Tetrabutylammonium perchlorate purissime (from Fluka) was used without further purification. All solutions were prepared from Milli-Q water.

All solutions were deaerated (for 50 min) by nitrogen. Nitrogen was allowed to flow over the solution at all times. All experiments were carried out at temperature $20 \pm 1 \text{ }^\circ\text{C}$.

3. Results and discussion

Fig. 1 compares two cyclic voltammograms (CVs) recorded for a thermally-induced Au(100)-(hex) electrode in $5 \cdot 10^{-2} \text{ M}$ KCl + $5 \cdot 10^{-4} \text{ M}$ TBAP (solid line) and, for the sake of comparison, in $5 \cdot 10^{-2} \text{ M}$ KCl alone (dotted line). The potential window from -0.780 V to $+0.610 \text{ V}$ is selected to encompass the various phase transitions and related features of significance here. The CV obtained for the $5 \cdot 10^{-2} \text{ M}$ KCl solution agrees well with the CVs which have been reported previously [10,12] for the reconstructed Au(100)-(hex) surface in the potential range between -0.750 V and -0.080 V , *i.e.* it depicts a small and almost potential independent current which corresponds to a low coverage of chloride followed by an increase in current leading to a large, high and irreversible peak R_E at -0.006 V , which is caused by the lifting of the hex-reconstruction. The region at more positive potentials represent the unreconstructed Au(100)-(1 × 1) surface with increasing chloride coverage, where at 0.550 V the spike E1 indicates a disorder/order transition within the adlayer or more

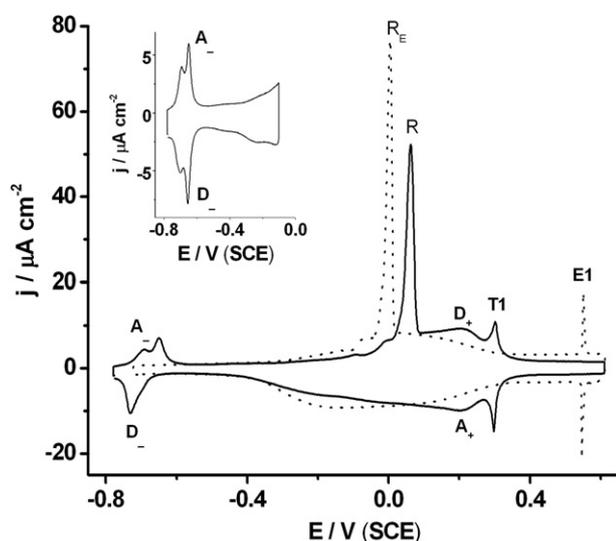


Fig. 1. CVs for thermally reconstructed Au(100)-(hex) in $5 \cdot 10^{-2} \text{ M}$ KCl (dotted line) and with addition of $5 \cdot 10^{-4} \text{ M}$ TBAP (solid line) in the whole double layer region. Inset: CV for thermally reconstructed Au(100)-(hex) surface in $5 \cdot 10^{-2} \text{ M}$ KCl + $5 \cdot 10^{-4} \text{ M}$ TBAP when the anodic limit of the first scan does not exceed the potential of the lifting of the reconstruction. Description of the peaks, humps and spikes is provided in the text.

precisely the formation of the incommensurate $c(\sqrt{2} \times p)$ R45° chloride adlayer [12]. We mention in passing that recently, the application of video-STM enabled finding also a $c(2 \times 2)$ structure at potentials slightly positive of that of zero charge [23]. Next, the CV recorded in the presence of $5 \cdot 10^{-4} \text{ M}$ TBAP exhibits a broad and split anodic hump A_- at *c.a.* -0.700 V corresponding to the adsorption of these cations at the reconstructed Au(100) surface, which reduces the double layer current till the onset of peak R at a positive value of potential (0.063 V) related to the lifting of the hex-reconstruction. Peak R is shifted by 69 mV to more positive potentials than those of R_E which means that the stability of the (hex) structure had increased owing to the hindering of the adsorption of Cl^- anions by TBA cations which would be expected to lift the reconstruction. The subsequent increase of potential depicts the voltammetric contour which does not follow monotonic decrease of current recorded in TBA-free solution but takes the form of a well-developed hump D_+ with the overlapping spike T1 at *c.a.* 0.302 V . Thus it seems likely that the appearance of hump D_+ may indicate significant but not complete (*vide infra*) desorption of TBA cations (in contrast to a continuous increase in Cl^- anions adsorption) from the unreconstructed surface. If so, it means that the above mentioned lifting of the reconstruction took place when TBA cations were present at the surface in the amount much greater than in perchlorate solution [8] in which partial desorption of these cations precedes this process. The adsorptive origin of hump D_+ is already partly concluded from the presence of its counterpart A_+ of a similar shape and at the same potential upon reversal of the sweep direction. The appearance of spike T1 upon the change of cation at much less positive potential than spike E1 is associated with a possible phase formation of a mixed ordered anion/cation adlayer on the surface. Incidentally, such a shift of spikes upon the change of cation has been already noticed for alkali cations at Au(100) [11]. Spike T1, likewise hump D_+ has the cathodic counterpart at almost the same potential because these voltammetric responses correspond to processes taking place already on the unreconstructed surface. In contrast, hump A_- has a counterpart D_- of different shape and potential indicating the structure sensitive adsorption of TBA cations as the adsorption and desorption of TBA cations occur at a reconstructed and an unreconstructed surface, respectively. However, when the potential window is restricted only to the range in which the (hex) structure is stable (see inset of Fig.1) CV depicts an anodic hump A_- which is nearly identical in shape to hump D_- during the negative scan at almost the same potential, showing additionally the reversibility of the adsorption/desorption of TBA cations on the reconstructed surface.

The substitution, in solution, of Cl^- anions by Br^- ones of stronger specific adsorption produces changes in the CVs. The changes are demonstrated in Fig.2 showing the CVs for a thermally-induced Au(100)-(hex) electrode in $5 \cdot 10^{-2} \text{ M}$ KBr + $5 \cdot 10^{-4} \text{ M}$ TBAP (solid line) and for comparison in the supporting electrolyte $5 \cdot 10^{-2} \text{ M}$ KBr alone (dotted line) are given. The latter CV depicts the reconstructing peak R_E not only higher and shifted to more negative potential, than in Cl^- solution, but also two spikes E1 and E2 which indicate the presence of incommensurate $c(\sqrt{2} \times p)$ R45° (at positive potentials) and commensurate $c(\sqrt{2} \times 2\sqrt{2})$ R45° structures [13,14], respectively. As follows from the former CV the TBA cations start to adsorb at (hex) surface (hump A_-) at the same potential as in electrolyte containing Cl^- anions, before the evolution of hydrogen. At less negative potentials, a reduction of the double layer current is observed and it retains this low value till -0.270 V , followed by large and high peak R assigned to the lifting of the reconstruction. The distance between the potentials of the reconstruction peaks R and R_E equal to 36 mV is smaller than for chloride, which indicates also an increase of the stability of the (hex) structure but to a lesser extent. This smaller shift means that the protection power of TBA cations is reduced with increasing adsorption of anions which would be expected to lift the reconstruction similarly as it has been observed for *e.g.* coumarin [24]. At less negative potentials a distinct hump D_+ caused by desorption of TBA cations from (1 × 1) surface (*vide supra*) is recorded. Its attribution to desorption of TBA

Download English Version:

<https://daneshyari.com/en/article/217921>

Download Persian Version:

<https://daneshyari.com/article/217921>

[Daneshyari.com](https://daneshyari.com)