Journal of Electroanalytical Chemistry 693 (2013) 1–8

Contents lists available at SciVerse ScienceDirect

Journal of Electroanalytical Chemistry

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

Lifting of the $(\sqrt{3}\times 22)$ surface reconstruction of Au(1 1 1) as a sensitive probe to monitor adsorption of cyclodextrin and its complexes in halide solutions

Scott N. Thorgaard, Philippe Bühlmann *

University of Minnesota, Department of Chemistry, 207 Pleasant St. SE, Minneapolis, MN 55455, United States

ARTICLE INFO

Article history:
Received 30 August 2012
Received in revised form 31 December 2012
Accepted 7 January 2013
Available online 23 January 2013

Keywords:
Single crystal electrochemistry
Surface reconstruction
Au(1 1 1)
Adsorption
Halide
Cyclodextrin

ABSTRACT

Stabilization of the $(\sqrt{3}\times 22)$ reconstruction of Au(1 1 1) in halide solutions by adsorbed, uncharged organic molecules was investigated using cyclic voltammetry. In aqueous solutions containing either iodide, bromide, or chloride, the presence of α-cyclodextrin (α-CD), β-cyclodextrin (β-CD), or a ferrocene inclusion complex of the latter (Fc·β-CD) was found to shift the potential of the $(\sqrt{3}\times 22)$ to (1×1) transition positive by several tens of mV. This shift is explained by the inhibition of halide adsorption due to the need to displace adsorbed cyclodextrin species. The size of the shift follows the trend in the strength of interaction between the three halides and the Au surface. Changes to the CV shapes suggest an influence of the cyclodextrins on both the thermodynamics and kinetics of the reconstruction lifting event. Differences observed in CVs recorded with the three cyclodextrin adsorbates also demonstrate the utility of the potential dependent surface reconstruction processes of Au(1 1 1) as a probe of adsorbed species. Each halide/cyclodextrin combination was further examined by perturbing the electrode surface with potential cycling and subsequently recording CVs to monitor the recovery of the surface to an equilibrium state.

1. Introduction

It is well known that the Au(1 1 1) surface becomes reconstructed by heating in vacuum or at ambient pressure, such as during the flame annealing commonly used to prepare Au(1 1 1) single crystals [1]. Relative to the Au(1 1 1) – (1×1) surface, the reconstructed Au(1 1 1) – $(\sqrt{3}\times 22)$ surface is compressed along a single [1 1 0] direction, with every 23rd surface atom in the same position as would be expected for a continuation of the underlying bulk lattice [2]. As a result, a regular pattern of raised ridges with a “herringbone” shape is formed [3]. Surface reconstructions have been observed for several crystal faces of Au, Pt, Ag, and other metals [2,4–7]. These surfaces reconstruct due to the differing interactions felt by surface atoms as compared to those in the bulk metal, with atoms moving to new positions in order to minimize surface energy. However, in liquid environments, the presence of adsorbed species on the surface may cause surface reconstructions to lift: favorable interactions with adsorbates allow metal atoms on the surface to return to their bulk positions. This phenomenon is strongly affected by the composition of the liquid phase, affinity of adsorbing species for the surface and, under electrochemical conditions, the applied potential. Thus, the inherent sensitivity of reconstruction processes to changes at the electrode/electrolyte interface allows them to act as useful probes of potential-dependent adsorption phenomena, both confirming the presence of adsorbing species and providing information as to the strength of interaction between the electrode and the adsorbate.

In particular, lifting of the Au(1 1 1) – $(\sqrt{3}\times 22)$ reconstruction to return the Au(1 1 1) – (1×1) surface in aqueous electrolyte solutions is strongly affected by the specific adsorption of anions [8–14]. At applied potentials far negative of the potential of zero charge (PZC), the surface coverage of anions is very low, and the reconstructed $(\sqrt{3}\times 22)$ surface is found. Anion adsorption increases sharply near the PZC, accompanied by lifting of the $(\sqrt{3}\times 22)$ reconstruction to yield the (1×1) surface [9]. The PZC for Au(1 1 1) and the potential at which the reconstruction is lifted vary in a wide range depending on the identity of the anion in solution, suggesting that differences between the energies of specific adsorption on reconstructed and unreconstructed surfaces play a dominant role in determining the potential at which reconstruction occurs or lifts [8].

The lifting of electrode surface reconstructions may also be affected by neutral, organic adsorbates. This has been investigated, e.g., for the lifting of the Au(1 0 0)–(hex) reconstruction in SO_4^{2-} and ClO_4^- solution, for which it was found that organic species such as pyridine adsorb onto the bare metal surface and influence the subsequent potential dependent adsorption of anions and, thereby, the lifting of the reconstruction [15–17]. Depending on the characteristics of the organic molecule, adsorbates were found to either

---

* Corresponding author. Tel.: +1 612 624 1431; fax: +1 612 626 7541.
E-mail address: buhlmann@umn.edu (P. Bühlmann).

1572-6657/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jelechem.2013.01.007

stabilize the reconstructed surface, shifting the lifting event to more positive potentials, or destabilize it, shifting the lifting event to more negative potentials.

Similar results were reported for Au(1 1 1) but are still limited in scope, as nearly all studies have been carried out in solutions containing anions with a low affinity for the surface. Studies in SO_4^{2-} and ClO_4^- solutions found a large influence of organic adsorbates on the stability of the Au(1 1 1) – $(\sqrt{3} \times 22)$ surface reconstruction due to the relatively weak interactions between the Au surface and perchlorate or sulfate anions [18–21]. One of the few studies with more strongly adsorbing anions showed that Triton X-100 stabilized the reconstructed Au(1 1 1) – $(\sqrt{3} \times 22)$ surface in the potential window of chloride adsorption [22]. There is also the special case of an organic species adsorbing at potentials positive of those where an ordered anion adlayer is present, wherein a monolayer is formed on top of an underlying anion adlayer. This has been demonstrated for a small number of compounds on iodide [23,24], bromide [25], and sulfate [26] modified Au(1 1 1). In studies of porphyrin monolayers on iodide and bromide modified Au(1 1 1), cyclic voltammograms in dilute halide solutions containing porphyrins showed alteration of peaks attributed to the lifting of the reconstruction, suggesting at least some competing adsorption of the porphyrins and halides [24,25]. However, to our knowledge, a systematic investigation of the influence of uncharged organic adsorbates on the $(\sqrt{3} \times 22)$ to (1×1) transition of Au(1 1 1) in solutions containing different specifically adsorbing anions has not been attempted.

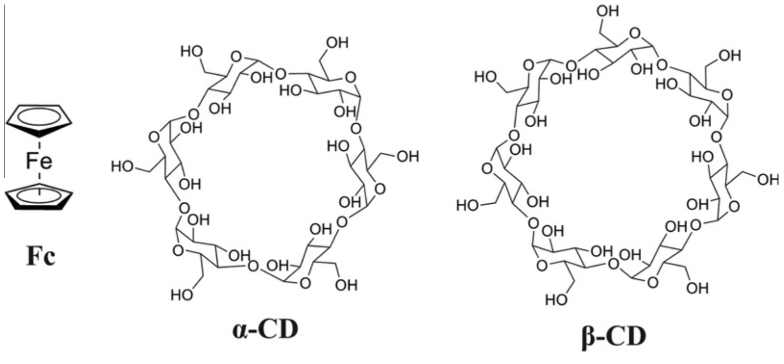
In this paper, we report on the use of cyclic voltammetry to investigate the effect of α- and β-cyclodextrin and a host–guest complex of the latter on the adsorption of three halides, i.e., Cl^-, Br^-, and I^-. The three halides were selected because their relative strengths of interaction with Au(1 1 1) follow a systematic trend, with iodide adsorbing more strongly than bromide, and bromide more strongly than chloride [9,10]. Unlike the more commonly used SO_4^{2-} or ClO_4^-, all three halides are known to interact strongly with Au(1 1 1), and we expected to observe significant potential-dependent competition for the surface between the halides and cyclodextrin species.

Cyclodextrins were selected as representative uncharged organic adsorbates for their solubility in water and the possibility of complex formation by inclusion of ferrocene within the cyclodextrin cavity. Cyclodextrins are macrocyclic oligosaccharides, with the α- and β-cyclodextrins consisting of six and seven glucose units, respectively (see structures in Scheme 1). Cyclodextrins have the shape of a barrel, with hydroxyl groups on the upper and lower rims, imparting high solubility in aqueous solution. The interior of the cyclodextrin cavity is hydrophobic, and for this reason cyclodextrins form inclusion complexes with hydrophobic species of appropriate size [27,28]. Following earlier investigations on liquid mercury electrodes [29–32], cyclodextrin adsorption has been examined on Au(1 1 1) surfaces in the absence of adsorbed anions in dilute $NaClO_4$ solution using in situ STM [33–35]. These studies found that the cyclodextrin monolayers formed ordered, "nanotube-like" structures over limited potential windows. While these authors did not examine the influence of cyclodextrins on the stability of the Au(1 1 1) – $(\sqrt{3} \times 22)$ reconstruction and performed their experiments in the absence of halides, we expected to find adsorption of cyclodextrins at potentials where the halide surface concentration was low, and we anticipated an influence of the cyclodextrins on the lifting of the Au(1 1 1) – $(\sqrt{3} \times 22)$ reconstruction in the presence of halides. Given earlier work with ordered porphyrin monolayers formed on halogen-modified Au, it appeared quite plausible that cyclodextrins would similarly form ordered potential dependent monolayers on halogen-modified electrodes. However, preliminary observations with in situ STM of β-CD on halogen–Au were unable to produce molecularly resolved images. It is possible that this is not related to the degree of lateral order in the CD monolayer but is an imaging artifact caused by the additive thicknesses of the β-CD and bromide adlayers. Therefore, we chose to focus here on investigations using voltammetry with Au(1 1 1) single crystals.

We were also interested to see whether formation of an inclusion complex with a cyclodextrin would alter adsorption characteristics enough to have a significant effect on either the lifting of the Au(1 1 1) – $(\sqrt{3} \times 22)$ reconstruction or the stability of the halide adlayer. Using the different cyclodextrins and the cyclodextrin inclusion complex as test cases, we have shown that beyond sole confirmation of the presence of an adsorbed organic species, the lifting of the reconstruction can also act as an indirect probe of the character of an adsorbate. Our goal here was to carry out an investigation of the potential dependence of the Au(1 1 1) reconstruction processes on the chemical identities of the different adsorbates involved.

2. Experimental

A Au(1 1 1) single crystal bead electrode purchased from Icryst (Jülich, Germany) served as the working electrode for all experiments. The bead had been cut parallel to the (1 1 1) face by techniques similar to those of Clavilier to expose a (1 1 1) surface roughly 2 mm in diameter [6]. All cyclic voltammetry was performed with the electrode in a hanging meniscus configuration [24,36], wherein the electrode is lowered into the electrolyte solution from above and then pulled back to create a contact between the solution and the (1 1 1) face. Prior to each experiment, the electrode was cleaned by heating in a hydrogen flame for 5 min, followed by cooling in air for 10 s. After cooling and prior to the transfer into the electrochemical cell, the electrode was protected from the ambient atmosphere by immersion into a droplet of pure water.



Scheme 1. Structures of ferrocene (Fc), α-cyclodextrin (α-CD), and β-cyclodextrin (β-CD).

A Ag/AgCl reference electrode (Bioanalytical Systems, West Lafayette, IN, USA; 3 M KCl filling solution, glass frit separation from the sample) and Pt wire auxiliary electrode were used for all experiments. All potentials in this work are quoted relative to this Ag/AgCl reference electrode. Cyclic voltammetry was performed using a CHI600C Electrochemical Analyzer (CH Instruments, Austin, TX, USA). All solutions were prepared with water deionized and charcoal treated with a Milli-Q Plus reagent grade purification system (Millipore, Bedford, MA, USA) and degassed with high purity argon under stirring for 30 min before each experiment. Unless stated otherwise, CVs did not show significant changes upon repeated scanning, and CVs shown are the second scan in a set of multiple scans.

Ferrocene (Fc), α-cyclodextrin (α-CD), and β-cyclodextrin (β-CD) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Ferrocene was recrystallized twice from ethanol before use, while α-CD and β-CD were used as received. Analytical reagent grade KI, KBr, and KCl were purchased from Mallinckrodt (St. Louis, MO, USA) and $KClO_4$ from G. Frederick Smith (Columbus, OH, USA).

Solutions containing β-CD and the inclusion complex Fc·β-CD were prepared as follows: 10 mL of electrolyte solution containing 2 mM β-CD and an excess of solid ferrocene was shaken for 3 h at room temperature, resulting in a transparent solution that still contained a large amount of undissolved ferrocene. The latter was then removed by careful decantation, and the liquid portion quantitatively transferred to another flask and diluted fivefold with additional electrolyte solution to ensure complete dissolution of any remaining ferrocene crystals. This produced a 0.40 mM β-CD solution containing a mixture of Fc·β-CD and uncomplexed β-CD.

The ratio of free β-CD and its Fc complex, Fc·β-CD, was estimated from the solubility of Fc and the stability of the complex. A binding constant of $1.65 \pm 0.04 \times 10^4$ has been reported for Fc with β-CD in pure water [37]. Considering the solubility of Fc in pure water, 4.25×10^{-5} mol/dm^3 [37], one predicts that in a solution of 2.0 mM β-CD saturated with Fc, 41% of the β-CD exists in the complexed form, Fc·β-CD. Were this solution diluted fivefold, as in our preparation of Fc-containing β-CD solutions, the resulting solution is predicted to contain 31 μM uncomplexed Fc and 0.4 mM β-CD in total, of which 35% exists as Fc·β-CD and 65% is free β-CD. (A more detailed derivation of these percentages is included in the Supporting Information.) While the Fc solubility and the stability of the Fc·β-CD complex in the $KClO_4$/halide solutions used here will differ somewhat from those in pure water, these numbers suggest that the Fc-containing β-CD solutions in our experiments contained a mixture of both Fc·β-CD and β-CD, with both the uncomplexed β-CD and the Fc complex at substantially higher concentrations than the free ferrocene.

3. Results and discussion

3.1. Voltammetry in the absence of cyclodextrins

Cyclic voltammograms (CVs) measured with Au(1 1 1) electrodes in contact with electrolyte solutions that contain specifically adsorbing anions (such as I^-, Br^-, Cl^-, and SO_4^{2-}) all have common features in the double layer potential region [11–14,38,39]. CVs for Au(1 1 1) electrodes immersed in aqueous solutions containing 20 mM $KClO_4$ as the supporting electrolyte and either 0.15 mM KI, 0.15 mM KBr, or 0.15 mM KCl are included in the Supporting Information. The sharp anodic peaks located at −0.35 V for the KI solution, +0.05 V for the KBr solution, and +0.25 V for the KCl solution each correspond to the lifting of the $(\sqrt{3} \times 22)$ reconstruction during halide adsorption near the PZC [9,13,38]. The shift in the PZC upon lifting of the reconstruction results in a sudden change in the double layer capacitance of the interface, and this sharp peak corresponds to the additional charging current [2]. The asymmetric shape of the peak and lack of an equally sharp feature in the return scan of the CV has been taken as evidence that the lifting of the reconstruction is a kinetically sluggish process consisting of multiple steps [39]. The broad, sloping features just positive of each sharp peak correspond to gradually increasing halide coverage, up to the maximum expected for a close packed monolayer [12,14,38,39]. Capacitive currents throughout this region are also convoluted with partial charge transfer current to the halide to form what is essentially a covalently bonded halogen monolayer on the electrode surface [9]. Therefore, these electrodes have been alternately referred to as "halogen modified" or "halide modified". Each CV also shows a smaller pair of peaks corresponding to an order/disorder transition within the halide adlayers [9,38,40] located at +0.30 V, +0.58 V, and +0.78 V for the KI, KBr, and KCl containing solutions, respectively.

Importantly, the position of the first sharp peak changes as a function of the strength of the interaction between the anion and the Au(1 1 1) surface, with the most strongly interacting ion, I^-, adsorbing and lifting the reconstruction at the most negative potential, followed by Br^- and Cl^- [9,10]. Furthermore, in the presence of 0.15 mM halide, there is effectively no contribution to the surface electrochemistry by ClO_4^-. To confirm this, we performed a limited number of CVs using 0.15 mM KBr solutions containing also 10 mM K_2SO_4 (not shown) and observed no significant difference from CVs obtained with 20 mM $KClO_4$. This was an expected result as sulfate, like perchlorate, does not interact with Au(1 1 1) nearly as strongly as do the halides [9,11,41].

3.2. Voltammetry with cyclodextrin adsorbates

The following sections describe CV experiments in solutions containing one of the potassium halides (KI, KBr, or KCl), both with and without the addition of 0.40 mM α-CD, β-CD, or a mixture including a Fc complex of the latter. For KBr and KCl, large changes in the CV were observed upon the introduction of cyclodextrin species. A much less pronounced effect was observed for KI. As explained in detail below, we attribute these changes to stabilization of the $Au(1\,1\,1) - (\sqrt{3} \times 22)$ reconstruction by the cyclodextrins, which are able to adsorb on the anion-free $Au(1\,1\,1) - (\sqrt{3} \times 22)$ surface. As the halides adsorb, they face an energy barrier arising from the need to displace the cyclodextrins from the metal surface. This results in a shift in the potential at which the $Au(1\,1\,1) - (\sqrt{3} \times 22)$ reconstruction is lifted, as well as a significant change in peak shapes for the entire "halide region" of the CV. For all the CVs recorded in solutions containing Fc or Fc·β-CD, no additional diffusion controlled peaks were observed within the potential windows used. Thus, neither the dissolved Fc·β-CD complex nor the dissolved free ferrocene give rise to a recognizable peak in the CV, and any alterations to the CV shape upon the addition of Fc·β-CD can be ascribed to surface phenomena.

Large current increases were seen for sweeps to potentials more positive than +0.9 V vs. Ag/AgCl, attributable to oxidative desorption of the halides and formation of gold oxide. Indeed, in our previous work with porphyrin monolayers on bromide modified Au(1 1 1), sweeps to potentials more positive than those needed to cause the formation of a gold oxide monolayer were found to completely desorb both the halide and the porphyrin from the surface [25]. In this work, we exploited this effect to probe differences between each set of adsorbates. For each solution, after CVs were initially recorded in the potential region below oxidation both of the gold surface and of the dissolved halides, additional CVs were performed with a switching potential of +1.5 V vs. Ag/AgCl. These scans reached the anodic solvent limit in 20 mM $KClO_4$, and large peaks corresponding to the formation and removal of gold oxide were seen. After this potential cycling (5 scans to +1.5 V at

40 mV/s), CVs were again recorded in the double layer region, i.e., between −0.7 and +0.1 V for KI solutions, between −0.6 and +0.7 V for KBr solutions, and between −0.1 and +0.9 V for KCl solutions. CV data immediately following potential cycling up to +1.5 V is somewhat difficult to interpret: the scans are complicated by the dynamic processes of adsorption and reorganization of species on the surface. However, significant differences were found between CVs following potential cycling in the presence and absence of cyclodextrins, and between CVs obtained with solutions of the three halides. These CVs offer several clues to the relative strengths of interaction between the Au surface, the cyclodextrins, and the three halides. Importantly, in all cases the CV shape eventually (20–50 min) returned to those seen before potential cycling was performed, and we conclude that the potential cycling described does not irrevocably change the electrode surface.

3.2.1. Voltammetry with bromide and cyclodextrin adsorbates

Fig. 1 shows CVs for Au(1 1 1) electrodes in contact with solutions containing 20 mM $KClO_4$, 0.15 mM KBr, and either no cyclodextrin, 0.40 mM α-CD, 0.40 mM β-CD, or 0.4 mM β-CD solutions which had been treated with Fc to give the inclusion complex, as explained above in Section 2. For the cyclodextrin-free case, we found that the large peak corresponding to the anion-induced lifting of the $\mathrm{Au}(1\,1\,1)-(\sqrt{3}\times 22)$ reconstruction is often split at its maximum into two very close peaks. In this case, the tallest maximum occurs at +0.062 V, with the other maximum at +0.042 V. This is consistent with previous reports on the $\mathrm{Au}(1\,1\,1)-(\sqrt{3}\times 22)$ to (1×1) transition, which found lifting of the reconstruction to be a multi-step process [9,22,42].

Several differences are seen in CVs recorded with the addition of the two uncomplexed cyclodextrins to the solution. Foremost, the peak corresponding to the lifting of the reconstruction is noticeably smaller and shifted by +22 mV for the 0.40 mM α-CD solution, and +34 mV for 0.40 mM β-CD. These shifts in peak position were highly reproducible (±2 mV) over repeat trials. Closer examination of these CVs reveals a small shoulder just negative of the peak maximum, while the maximum itself is not split as for the cyclodextrin-free case. (The Supporting Information contains an expanded version of Fig. 1, highlighting changes in the reconstruction lifting peak.) This change consists of not only a shift of the reconstruction peak to a more positive potential, but also a change in the ratio of the heights of the maxima. Similar to interpretations of the effect of organic adsorbates on the lifting of the Au(1 0 0)–(hex) reconstruction [15–17], we attribute this positive shift in the potential of reconstruction to stabilization of the reconstructed surface by adsorbed cyclodextrins at potentials where the bromide surface concentration is low. The necessity of displacing the cyclodextrin poses an additional thermodynamic barrier to anion adsorption, resulting in a positive shift of the reconstruction peak. The presence of cyclodextrin on the surface as bromide starts to adsorb also affects the kinetics of bromide adlayer formation, as reflected in the changes to the CV shape relative to the cyclodextrin-free case.

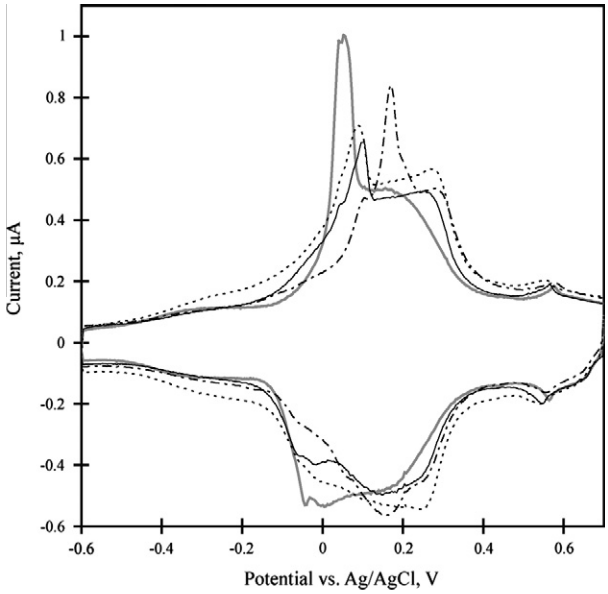


Fig. 1. CVs recorded for Au(1 1 1) electrodes in solutions containing 20 mM $KClO_4$ and 0.15 mM KBr (thick gray line), and with the addition of either 0.40 mM α-CD (dotted line), 0.40 mM β-CD (solid black line), or 0.40 mM β-CD loaded with ferrocene (dashed line). The scan rate for all CVs was 40 mV/s.

Beyond the reconstruction peak, there is also a significant change in the broad region corresponding to maximization of the bromide coverage, i.e., the potential range just positive of the reconstruction peak and extending to roughly +0.4 V. The CV features here have become slightly compressed along the potential axis, with a differently sloped shape that is roughly symmetrical in the return sweep. As with the alteration of the reconstruction peak shape, we attribute this change too to inhibition of anion adsorption by the presence of cyclodextrins.

In a supporting experiment, a CV in the presence of 4 mM β-CD found the reconstruction lifting peak shifted positive by a further 27 mV, making it apparent that there is a dependence of this effect on the cyclodextrin concentration (see Supporting Information). However, as explained below, the effect of adsorbing cyclodextrins varied beyond simple shifting of peaks for the iodide and chloride systems. Therefore, while the combined effects of stabilization of the reconstructed surface by cyclodextrins and destabilization by the halide suggest interdependence on their respective concentrations, a complete description of these concentration interdependences for all of the halide/CD combinations discussed is beyond the scope of this work. We have instead undertaken an investigation to probe chemical differences between the different halides and CD species, and have fixed the concentrations of the halide and CD concentrations for all experiments at convenient (but arbitrary) values of 0.15 mM and 0.4 mM, respectively.

The relatively small difference between the α- and β-CD cases suggests that the two cyclodextrins possess similar adsorption characteristics on Au(1 1 1). In CVs using increasingly positive switching potentials up to +1.5 V, no peaks were seen in the presence of cyclodextrin that were not already observed with cyclodextrin-free solutions. This suggests that either the cyclodextrin does not re-adsorb atop the bromine monolayer, or that the adsorbed cyclodextrin is not oxidized in this potential window. This contrasts observations by Ohira and co-workers, who observed the oxidation of cyclodextrins at positive potentials on bare Au(1 1 1) [33–35]. The small differences in charging current for regions below −0.3 V or above +0.4 V may reflect variability due to a small degree of unavoidable wetting of the bead sides when these hanging meniscus CVs were measured.

We also sought to probe what effect, if any, inclusion of a guest molecule into the cyclodextrin cavity would have on the Au(1 1 1) reconstruction. In a strict sense, there is no such thing as an "empty" cyclodextrin cavity in aqueous solution; the cavity is always populated either by water molecules or electrolyte (more often anions than cations) [27,43]. However, hydrophobic molecules with compatible dimensions can displace the cavity occupants and form host–guest complexes with cyclodextrins. Here, we chose as the guest molecule unsubstituted ferrocene (Fc, see structure in Scheme 1), which with its 1:1 binding constant of $(1.65 \pm 0.04) \times 10^4$ is known to have a high affinity for β-CD [44,45]. α-CD and Fc also form inclusion complexes, albeit with much weaker binding. The binding constants for 1:1 and 2:1 complexes of α-CD and Fc in pure water are $(1.39 \pm 0.21) \times 10^2$ and $(2.36 \pm 0.06) \times 10^3$, respectively [46].

The dashed trace in Fig. 1 shows a CV recorded in a solution containing 20 mM $KClO_4$ with 0.15 mM KBr and 0.40 mM β-CD loaded with ferrocene, as explained in Section 2 above. The current maximum associated with the lifting of the $Au(111) - (\sqrt{3} \times 22)$ reconstruction is located at +0.170 V, i.e., it is shifted by +108 mV vs. the cyclodextrin-free case and +74 mV vs. the CV for a ferrocene-free solution of β-CD. In a control experiment, CVs recorded in electrolyte solutions treated with ferrocene identically to the above but in the absence of β-CD were identical to CVs recorded in solutions containing only the halide and supporting electrolyte, confirming that there is no substantial effect of uncomplexed ferrocene in the experiments with Fc·β-CD solutions (see Supporting Information). Clearly, addition of the Fc·β-CD inclusion complex to the solution has a major effect on bromide adsorption and lifting of the reconstruction. Considering the 108 mV shift in the reconstruction lifting peak in the presence of Fc·β-CD (vs. a 34 mV shift with β-CD alone), it is evident that the interaction between the surface and the Fc·β-CD complex is stronger than for uncomplexed β-CD. The positive potential shift of the lifting of the reconstruction here indicates that regardless of the surface concentration of either species, Fc·β-CD stabilizes the reconstructed surface to a greater extent than uncomplexed β-CD. This suggests that the ferrocene moiety in Fc·β-CD interacts more strongly with the Au surface than the water present in the uncomplexed β-CD cavities, which appears to be an electronic effect. For solutions containing only KBr and $KClO_4$, CVs immediately following potential cycling to +1.5 V showed a slight increase (5%) in the height of the reconstruction lifting peak, but there were otherwise no differences from the CV shown in Fig. 1. Potential-induced surface reconstruction is known to proceed by nucleation steps [2,42] and this slight increase in peak current may be due to an increased number of nucleation sites (defects) generated by the repeated formation and removal of a gold oxide monolayer during potential cycling. In contrast, marked differences can be seen between CVs taken before and immediately after potential cycling in solutions containing 20 mM $KClO_4$, 0.15 mM KBr, and either 0.40 mM α-CD or 0.40 mM β-CD. Fig. 2 shows six CV scans from three sets of experiments: The dotted traces in panels (a) (0.40 mM α-CD), (b) (0.40 mM β-CD), and (c) (0.40 mM Fc treated β-CD) were recorded before potential cycling, and are identical to CVs presented in Fig. 1. The solid traces in each panel were recorded immediately after potential cycling to +1.5 V, as outlined above. In each case, significant shifting and splitting of some of the CV features are seen following potential cycling. This is most dramatic for α-CD, where the peak for the lifting of the Au reconstruction is split into two large peaks separated by over 100 mV. In all cases, the CV shapes returned to those shown in Fig. 1 after 20 min. This recovery occurred both when scanning was performed continuously over 20 min as well as when the electrode was left at the open circuit potential for an equal amount of time. Because the CV shapes following potential cycling were continually changing over several minutes, it was not possible to characterize the additional peaks by varying the scan rate and measuring peak heights. However, it seems reasonable to conclude that these CVs reflect a surface undergoing dynamic rearrangement following adsorption of both cyclodextrins and bromide after desorption during potential cycling.

The CV that followed potential cycling in bromide solution containing Fc-treated β-CD (solid trace in panel (c) of Fig. 2) showed some additional transient features not found in the other systems. Following potential cycling to +1.5 V, the CV is complicated by two large peaks at −0.54 and −0.08 V. While a comparison of the baselines in the solid and dotted line traces suggests that these peaks are associated with a surface process, these peaks were found to decrease in height after several scans, making it difficult to acquire useful data confirming the surface nature of the underlying process(es) by their scan rate dependence. With continued scanning, the CV shape eventually returned to one indistinguishable from the pre-potential cycling CV, suggesting complete recovery of the surface. Because no similar peaks were seen in the absence of Fc·β-CD, we associate these features with an effect of Fc·β-CD. A redox product of Fc·β-CD may be generated during the potential cycling, which eventually would desorb and diffuse away from the electrode surface upon continued scanning.

3.2.2. Voltammetry with iodide and cyclodextrin adsorbates

Fig. 3 shows CVs recorded in 20 mM $KClO_4$ solution containing 0.15 mM KI, and either no cyclodextrin, 0.40 mM α- or β-CD, or 0.40 mM β-CD treated with Fc, as explained in Section 2. Similar to the bromide case, the tall peak associated with the lifting of the reconstruction at −0.35 V shifts to a slightly more positive potential (+35 mV for 0.4 mM α-CD, and +11 mV for 0.4 mM β-CD), accompanied by a change in the overall shape of the CV and the relative peak heights. Again, we attribute this difference to stabilization of the reconstructed surface by adsorbed α- or β-CD. We interpret the relative subtlety of the effect as compared to the bromide case as a reflection of the strength of the I–Au interaction, which is stronger than it is in the case of the other halides, resulting in a decreased effect of the CD on the CVs. For solutions containing a cyclodextrin, the first CV scans recorded immediately after making contact between the electrode and the electrolyte

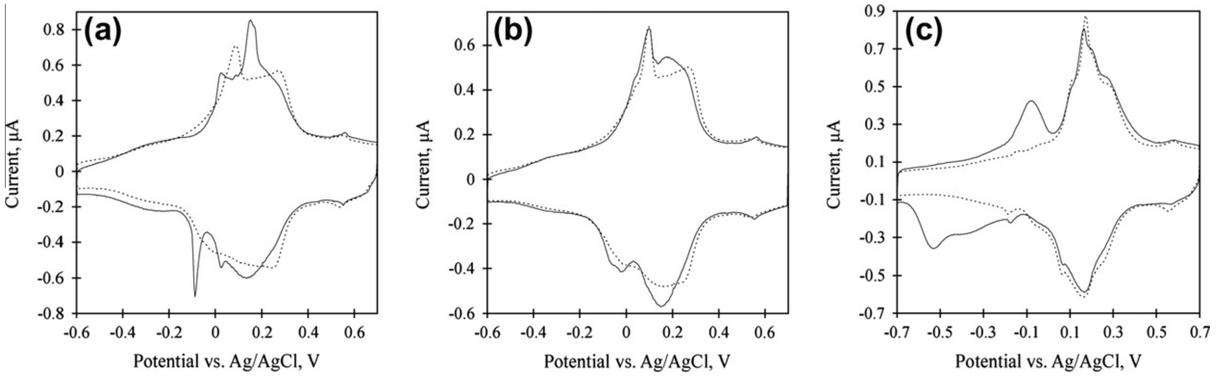


Fig. 2. CVs recorded for Au(111) electrodes in solutions containing 20 mM $KClO_4$, 0.15 mM KBr, and either (a) 0.40 mM α-CD, (b) 0.40 mM β-CD, or (c) 0.40 mM ferrocene-treated β-CD. Dotted traces were recorded *before* potential cycling, while solid line traces were recorded *immediately after* potential cycling to +1.5 V. The scan rate for all CVs was 40 mV/s.

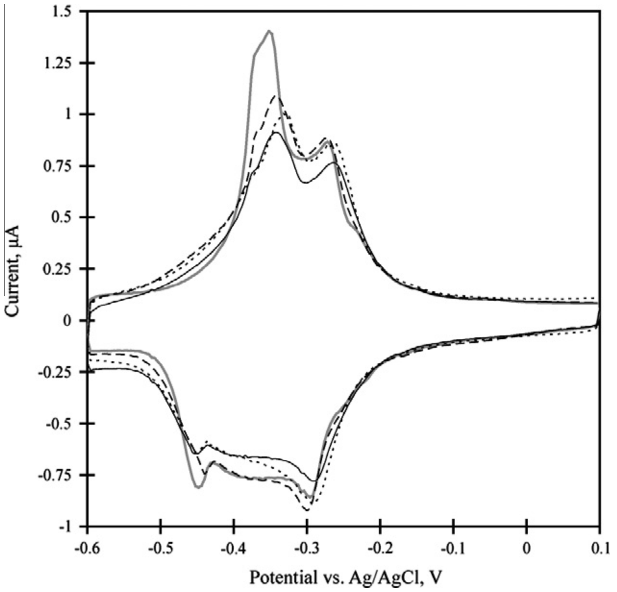


Fig. 3. CVs recorded for Au(1 1 1) electrodes in 20 mM KClO$_4$ with 0.15 mM KI (thick gray), and following the addition of either 0.40 mM α-CD (dotted), 0.40 mM β-CD (solid), or 0.40 mM Fc-treated β-CD (dashed). The scan rate for all CVs was 40 mV/s.

solution were nearly identical to the CVs from the cyclodextrin-free case, and only after approximately 45 min in solution did the CV shapes change fully to those shown in Fig. 3 for cyclodextrin solutions in equilibrium with the electrode. No similar change in the CV shape with time was observed for the cyclodextrin-free system. That the initial CV scans with cyclodextrins resembled the cyclodextrin-free case, and that more time was required to reach an equilibrium CV shape than for the bromide system, indicates an overall weaker influence of α- and β-CD on the iodide adlayer.

Unlike CVs following potential cycling in solutions containing bromide and cyclodextrins, which showed unique, transient shapes, CVs immediately following potential cycling in solutions containing iodide and either α- or β-CD resembled closely CVs taken in the absence of cyclodextrin, with gradual transformation of the CV shape with repeated scanning. A representative 30-cycle CV immediately following potential cycling up to +1.5 V in solutions containing 20 mM KClO$_4$, 0.15 mM KI, and 0.40 mM α-CD is shown in the Supporting Information. For these multi-cycle CVs, the peak current for the reconstruction lifting event decreased by roughly 20% in successive cycles, accompanied also by a shift in the peak potential and a change in the relative heights of the reconstruction peak and the second peak associated with further iodide adsorption. This slow transformation of the CV shape is similar to what was observed following initial contact with the electrolyte solution. A nearly identical trend was observed for the experiments with β-CD and Fc-treated β-CD. We interpret this transient behavior (an immediate return to the "CD-free" CV shape followed by gradual changes) as an indication that surface behavior is affected more strongly by the halide in the iodide/cyclodextrin system relative to the bromide or chloride cases. In control experiments, CVs in the same electrolyte solution but in the absence of cyclodextrin showed only a ~5% decrease in the peak current over 30 cycles following potential cycling, with no shifting of the peak potential.

CVs recorded in iodide solution but with Fc-treated β-CD also showed a much less dramatic effect of the cyclodextrin than in the analogous experiment in bromide solution. The presence of ferrocene-treated β-CD in the cell resulted in a decrease in the height of the reconstruction lifting peak, as well as a shift in the peak potential. However, the shift in the peak potential was nearly the same as that observed for solutions containing β-CD without ferrocene (around 10 mV). Immediately after potential cycling to +1.5 V, there was a return to the CV shape observed in the absence of β-CD, followed by a slow transformation to the CV shape shown in the dashed trace, echoing exactly the behavior described above (and shown in the Supporting Information) for potential cycling in an α-CD solution. Interestingly, the two larger peaks found after potential cycling in bromide/Fc·β-CD solution (see Fig. 2) were not found for the iodide system, suggesting that the strongly adsorbed iodide layer present in that potential region protects the surface or otherwise prevents that surface process from occurring. The apparent lack of additional effects from the inclusion of Fc into the β-CD is consistent with the interpretation that the influence of cyclodextrins on halide adsorption is the weakest for the iodide system because this anion interacts more strongly with Au(1 1 1) than bromide and chloride.

3.2.3. Voltammetry with chloride and cyclodextrin adsorbates

Of the three halides, the most dramatic effects in the presence of cyclodextrin were seen for solutions containing chloride. Fig. 4 shows CVs taken in 20 mM KClO$_4$ with 0.15 mM KCl, with and without either 0.40 mM α- or β-CD, or 0.4 mM β-CD treated with Fc, as explained in Section 2. In the CV in the absence of cyclodextrin, we see the familiar halide shape with a large peak at +0.25 V corresponding to the lifting of the reconstruction. The pronounced splitting of the peak was somewhat unexpected considering CVs described in the literature [12,22,47] However, we did notice that the peak decreased in size and that the splitting became less pronounced with many successive CV cycles.

Considerably different CVs were recorded in the presence of 0.40 mM cyclodextrin solutions. For the case of α-CD, the split peak at +0.25 V seen for the CD-free case is replaced by a much smaller peak at +0.29 V as well as a tall, very sharp peak at +0.39 V. Assuming that the majority of the reconstruction lifting process takes place at the sharp peak, this would constitute a shift in the reconstruction lifting potential of +140 mV. This suggests a large stabilization of the Au(1 1 1) – $(\sqrt{3}\times 22)$ reconstruction by cyclodextrin adsorbates in the presence of chloride. Moreover, the sharp peak is

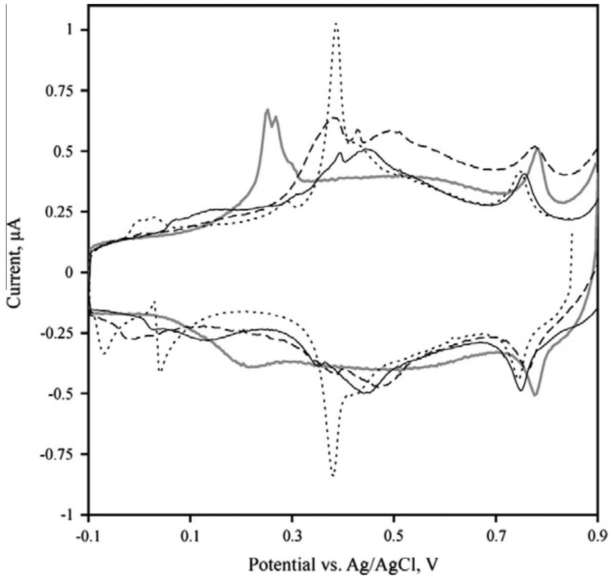


Fig. 4. CVs recorded for Au(1 1 1) electrodes in 20 mM KClO$_4$ with 0.15 mM KCl (thick gray), and with the addition of either 0.40 mM α-CD (dotted), 0.40 mM β-CD (solid), or 0.40 mM Fc-treated β-CD (dashed). The scan rate for all CVs was 40 mV/s.

followed by a very symmetric return peak in the opposing scan of the CV. This degree of symmetry is not observed with any of the other halide/CD combinations, and suggests a significant alteration of halide adsorption and surface reconstruction kinetics by α-CD.

Beyond the changes to the reconstruction peaks, multiple smaller peaks appeared between −0.1 and +0.1 V. Because these features show a linear dependence of peak height on the scan rate, we attribute them to structural transitions within the CD adlayer, likely related to a changing surface coverage by adsorbed CD. That we do not see similar peaks in the bromide and iodide cases is probably due to the much lower surface concentration of chloride in this potential region, consistent with the lower affinity of the chloride for the Au(1 1 1) surface. Lastly, the peaks assigned above to the formation of an ordered chloride monolayer were found to shift negative by roughly 35 mV in the presence of CD. The CV shown for the solution containing 0.40 mM β-CD shares features in common with the α-CD case, most notably the broad, symmetric feature at +0.46 V and the shift of the order/disorder transition of adsorbed chloride. However, the sharp peak at +0.40 V, presumably attributable to the lifting of the reconstruction, is now much smaller in the case of β-CD. This may indicate that for β-CD the reconstruction lifting event is spread over a wider potential range than in the case of α-CD. Moreover, comparing the α-CD with the β-CD case, there is a significant difference in the surface capacitance in the region between +0.1 and +0.3 V. The larger differences between the CVs obtained with the two cyclodextrins in chloride solution vs. the analogous iodide and bromide experiments may reflect the comparatively weak strength of the Cl–Au interaction; as the effect of adsorbed cyclodextrins on halide adsorption becomes larger, the differences between the two cyclodextrin species become more pronounced.

CVs recorded in 20 mM $KClO_4$ with 0.15 mM KCl and 0.40 mM Fc-treated β-CD again show significant differences from CVs recorded in solutions containing β-CD that had not been treated with ferrocene. As seen in the dashed trace in Fig. 4, the symmetric shape as well as the small sharp peak (both attributed above to lifting of the reconstruction during chloride adsorption in the presence of β-CD; features centered at roughly +0.43 V of the solid trace in Fig. 4) are now shifted further positive by roughly 50 mV. This shift is about 24 mV smaller than in the bromide/Fc·β-CD case, suggesting that the systematic trend in strengths of interaction between the halides and Au(1 1 1) is not the sole factor determining the relative influence of two different competing adsorbates on the lifting of the reconstruction.

There is also an additional large peak seen at +0.39 V in the dotted trace in Fig. 4 that was not seen in the absence of Fc·β-CD, suggesting a complicated influence on the surface reconstruction/lifting events by the competing adsorption of Fc·β-CD and β-CD with chloride. It is also possible that this additional peak is due to the oxidation of complexed ferrocene in surface adsorbed Fc·β-CD. However, it is difficult to distinguish these two possibilities given the large number of convoluted surface controlled peaks in the CV. The smaller peaks observed below +0.25 V in CVs recorded in chloride solution in the presence of β-CD without ferrocene also shifted upon the addition of Fc·β-CD, suggesting at least some difference in the thermodynamics or kinetics of the adsorption of Fc·β-CD and uncomplexed β-CD to the reconstructed electrode surface. Finally, the set of order/disorder transition peaks near +0.78 V shifts negative by roughly 30 mV upon addition of the cyclodextrin species, indicating that the ordered chloride monolayer on the surface is stabilized in the presence of cyclodextrin relative to the cyclodextrin-free case.

The response of the chloride-containing system to potential cycling was also distinctive. Unlike in the bromide and iodide systems, CVs recorded immediately following potential cycling to +1.5 V in solutions containing 20 mM $KClO_4$, 0.15 mM KCl, and either α-CD, β-CD, or Fc-treated β-CD showed essentially no change compared to CVs taken before potential cycling other than a slight increase (∼5%) in peak heights, as it was seen in all of the CD-free voltammograms upon potential cycling. It is likely that this reflects a faster establishment of equilibrium conditions at the electrode surface following desorption of the adsorbed species during potential cycling in chloride solution than for bromide and iodide. As a whole, these experiments show that the influence of cyclodextrin on the anion-induced lifting of the reconstruction of Au(1 1 1) is greater in chloride containing solutions than for either of the other halide systems examined, reflecting the weaker affinity of chloride for the Au surface relative to the other halides examined.

4. Conclusions

α- and β-CD as well as β-CD complexes of Fc were all found to stabilize the Au(1 1 1) − $(\sqrt{3} \times 22)$ reconstruction in aqueous solutions containing 20 mM $KClO_4$ and 0.15 mM halide. The cyclodextrins adsorb onto the unreconstructed surface at negative potentials and inhibit the adsorption of halides, which are known to strongly influence the potential at which the reconstruction is lifted to return to the Au(1 1 1) − (1×1) structure [9]. For the three halides used, i.e., chloride, bromide, and iodide, the inhibiting effect exhibited by the cyclodextrins was found to be the strongest in chloride containing solutions, and weakest in iodide containing solutions. This correlates with the relative strengths of interaction between Au(1 1 1) and these halides, which are known to be strongest for iodide and weakest for chloride. All three halide/cyclodextrin systems were also found to have unique responses to perturbation by potential cycling up to +1.5 V, exposing a relationship between the strength of interactions and the surface recovery processes following desorption of adsorbed species. Based on CV scans recorded immediately after potential cycling, the surface recovery appeared to kinetically favor halide adsorption for the iodide/cyclodextrin system, and cyclodextrin adsorption in the chloride/cyclodextrin system. On the other hand, in the bromide/cyclodextrin case, the marked transient behavior seen in CVs following potential cycling suggests a more even competition between the halide and the cyclodextrin during surface recovery.

A comparison between the CVs recorded in bromide and chloride solutions containing either β-CD alone or both β-CD and its inclusion complex with ferrocene (Fc·β-CD) suggests that Fc·β-CD is more effective at inhibiting halide adsorption on Au(1 1 1) than β-CD. Furthermore, based on the significantly larger effect on the lifting of the reconstruction observed in solutions containing Fc·β-CD and β-CD, as compared to solutions of β-CD alone, we also conclude that Fc·β-CD has a greater affinity for the Au(1 1 1) − $(\sqrt{3} \times 22)$ surface than does β-CD. The apparent lack of an additional effect of Fc·β-CD in iodide containing solutions is consistent with our conclusion that iodide adsorption dominates surface behavior in the iodide/cyclodextrin system due to the strength of the I–Au interaction.

In summary, the anion-induced lifting of the Au(1 1 1) − $(\sqrt{3} \times 22)$ reconstruction has been shown here to be useful in probing not only the presence of an adsorbed organic species on the Au(1 1 1) surface, but also the character of the adsorbate in that the magnitude of the shift in the reconstruction lifting event was found to vary with the nature of the organic species.

Acknowledgment

This work was supported by the National Science Foundation (EXP-SA 0730437).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jelechem.2013.01.007.

References

[1] D.M. Kolb, A.S. Dakkouri, N. Batina, The surface structure of gold single-crystal electrodes, in: A.A. Gewirth, H. Siegenthaler (Eds.), Nanoscale Probes of the Solid/Liquid Interface, Kluwer Academic Publishers, Dordrecht, Netherlands, 1995, pp. 263–284.
[2] D.M. Kolb, Prog. Surf. Sci. 51 (1996) 109–173.
[3] J.V. Barth, H. Brune, G. Ertl, Phys. Rev. B: Condens. Matter 42 (1990) 9307–9318.
[4] D.M. Kolb, J. Schneider, Electrochim. Acta 31 (1986) 929–936.
[5] A. Hamelin, J. Electroanal. Chem. 407 (1996) 1–11.
[6] J. Clavilier, R. Faure, G. Guinet, R. Durand, J. Electroanal. Chem. 107 (1980) 205–209.
[7] Y. Tang, L.J. Simpson, T.E. Furtak, Phys. Rev. Lett. 67 (1991) 2814–2817.
[8] A. Hamelin, J. Electroanal. Chem. 142 (1982) 299–316.
[9] J. Lipkowski, Z. Shi, A. Chen, B. Pettinger, C. Bilger, Electrochim. Acta 43 (1998) 2875–2888.
[10] O.M. Magnussen, Chem. Rev. 102 (2002) 679–726.
[11] Z. Shi, J. Lipkowski, M. Gamboa, P. Zelenay, A. Wieckowski, J. Electroanal. Chem. 366 (1994) 317–326.
[12] Z. Shi, J. Lipkowski, J. Electroanal. Chem. 403 (1996) 225–239.
[13] Z. Shi, J. Lipkowski, S. Mirwald, B. Pettinger, J. Chem. Soc., Faraday Trans. 92 (1996) 3737–3746.
[14] A. Chen, Z. Shi, D. Bizzotto, J. Lipkowski, B. Pettinger, C. Bilger, J. Electroanal. Chem. 467 (1999) 342–353.
[15] U.W. Hamm, D.M. Kolb, J. Electroanal. Chem. 332 (1992) 339–347.
[16] F. Henglein, D.M. Kolb, L. Stolberg, J. Lipkowski, Surf. Sci. 291 (1993) 325–336.
[17] P. Skoluda, U.W. Hamm, D.M. Kolb, J. Electroanal. Chem. 354 (1993) 289–294.
[18] T. Dretschkow, A.S. Dakkouri, T. Wandlowski, Langmuir 13 (1997) 2843–2856.
[19] Z. Li, B. Han, L.J. Wan, T. Wandlowski, Langmuir 21 (2005) 6915.
[20] S. Wu, J. Lipkowski, O.M. Magnussen, B.M. Ocko, T. Wandlowski, J. Electroanal. Chem. 446 (1998) 67–77.
[21] D. Yang, J. Lipkowski, Langmuir 10 (1993) 2647–2653.
[22] D. Krznarić, Electroanalysis 14 (2002) 657–664.
[23] M. Kunitake, N. Batina, K. Itaya, Langmuir 11 (1995) 2337–2340.
[24] S.N. Thorgaard, P. Bühlmann, J. Electroanal. Chem. 664 (2012) 94–99.
[25] S.N. Thorgaard, P. Bühlmann, Langmuir 26 (2010) 7133–7137.
[26] S. Yoshimoto, T. Sawaguchi, J. Am. Chem. Soc. 130 (2008) 15944–15949.
[27] J. Szejtli, Cyclodextrins and Their Inclusion Complexes, Akadémiai Kiadó, Budapest, 1982.
[28] J. Szejtli, Chem. Rev. 98 (1998) 1743–1753.
[29] Y. Matsui, H. Sawada, K. Mochida, Y. Date, Bull. Chem. Soc. Jpn. 48 (1975) 3446–3449.
[30] Z. Borkowska, J. Electroanal. Chem. 246 (1988) 423–431.
[31] R.K. Jaworski, M. Golęnzinowski, Z. Galus, J. Electroanal. Chem. 252 (1988) 425–440.
[32] M. Golęnzinowski, J. Electroanal. Chem. 267 (1989) 171–189.
[33] A. Ohira, T. Ishizaki, M. Sakata, M. Kunitake, I. Taniguchi, C. Hirayama, J. Electroanal. Chem. 472 (1999) 163–167.
[34] A. Ohira, T. Ishizaki, M. Sakata, I. Taniguchi, C. Hirayama, M. Kunitake, Colloids Surf., A 169 (2000) 27–33.
[35] A. Ohira, M. Sakata, I. Taniguchi, C. Hirayama, M. Kunitake, J. Am. Chem. Soc. 125 (2003) 5057–5065.
[36] D. Dickertmann, F.D. Koppitz, J.W. Schultze, Electrochim. Acta 21 (1976) 967–971.
[37] J.S. Wu, K. Toda, A. Tanaka, I. Sanemasa, Bull. Chem. Soc. Jpn. 71 (1998) 1615–1618.
[38] O.M. Magnussen, B.M. Ocko, J.X. Wang, R.R. Adzic, J. Phys. Chem. 100 (1996) 5500–5508.
[39] B.M. Ocko, O.M. Magnussen, R.R. Adzic, J.X. Wang, J. Lipkowski, J. Electroanal. Chem. 376 (1994) 35–39.
[40] X. Gao, G.J. Edens, M.J. Weaver, J. Electroanal. Chem. 376 (1994) 21–34.
[41] D.A. Scherson, D.M. Kolb, J. Electroanal. Chem. 176 (1984) 353–357.
[42] Y.-F. Liu, Y.-L. Lee, Y.-C. Yang, Z.-Y. Jian, W.-P. Dow, S.-L. Yau, Langmuir 26 (2010) 13263–13271.
[43] R.V. Chamberlain, K. Slowinska, M. Majda, P. Bühlmann, H. Aoki, Y. Umezawa, Langmuir 16 (2000) 1388–1396.
[44] A. Harada, S. Takahashi, J. Inclusion Phenom. 2 (1984) 791–798.
[45] A. Harada, Y. Hu, S. Yamamoto, S. Takahashi, J. Chem. Soc. Dalton Trans. (1988) 729.
[46] J.S. Wu, K. Toda, A. Tanaka, Bull. Chem. Soc. Jpn. 71 (1998) 1615–1618.
[47] S. Ye, I. Chikara, K. Uosaki, Langmuir 15 (1999) 807–812.