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The structure of the electrochemical double layer: Ag(111) in alkaline electrolyte

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ABSTRACT

The structure of the electrochemical double layer at the interface between a Ag(111) electrode and 0.1 M KOH electrolyte has been probed using in-situ surface X-ray scattering (SXS). Detailed modeling of the SXS data at negative potential ($E = -1.0$ V versus SCE) is consistent with the presence of an hydrated K^+ cation layer at a distance of 4.1 ± 0.3 Å from the Ag surface and at positive potential ($E = -0.2$ V), indicates that the presence of OH_{ad} stabilizes the hydrated K^+ cations through a non-covalent interaction forming a compact double layer structure in which the Ag-K^+ distance is reduced to 3.6 ± 0.2 Å.

1. Introduction

The design and synthesis of energy efficient and stable electrochemical interfaces (materials and double layer components) for accelerating and directing chemical transformations is the key to developing new alternative energy systems — fuel cells, electrolyzers and batteries [1,2]. In aqueous electrolytes, depending on the nature of the reacting species, the supporting electrolyte and the metal electrodes, two types of interactions have traditionally been considered: (i) direct — covalent bond formation between adsorbates and electrodes, involving chemisorption, electron transfer and release of the ion hydration shell; and (ii) relatively weak non-covalent metal-ion forces that may affect the concentration of ions in the vicinity of the electrode but do not involve direct metal-adsorbate bonding. The latter type of interactions are characteristic for the alkaline environment and it has been shown that the interaction of covalently bonded OH and alkali hydrated cations on Pt electrodes leads to the formation of OH-cation complexes with the locus centered in the compact part of the double layer [3]. Although these findings have established the importance of non-covalent interactions in surface chemistry, many important questions from the previous studies have remained open; a central issue being the determination of the position of hydrated cation clusters in the compact part of the double layer.

Surface X-ray scattering (SXS) is an ideal technique for probing the atomic structure at the electrochemical interface [4,5]. By combining specular crystal truncation rod (CTR) results (where the momentum transfer, **Q**, is entirely along the surface normal direction) with non-specular CTR results (where **Q** has an additional in-plane component) it is possible to probe both the termination of the crystal lattice and layer ordering above the interface, i.e. in the electrolyte layer, where the species are incommensurate with the underlying crystal lattice. Using this technique to study the Ag(111) electrode surface in non-adsorbing electrolyte (0.1 M NaF), Toney et al. proposed the presence of a dense ice-like layer of water adjacent to the interface and the flipping of the water molecule dependent on the applied electric field [6]. Very recently, Nakamura et al. showed that hydrated Cs^+ cations were present on top of a specifically-adsorbed Br adlayer on Ag(100) [7].

In this communication we present an in-situ SXS study of Ag(111) in 0.1 M KOH electrolyte. While there has been widespread study of multilayer oxide growth on Ag electrode surfaces, there has been less study of the underpotential region of oxidation, in spite of the fact that this is the potential region of oxygen and hydrogen peroxide reduction [8–11]. By measurement of the CTR's at fixed electrode potentials, a model of the layering at the interface is obtained.

2. Experimental details

The Ag(111) single crystal electrode (miscut<0.2°) was prepared by cycles of sputtering and annealing in the UHV surface characterization laboratory (SCL) at the ESRF. After a sharp (1x1) LEED pattern was obtained, the crystal was transferred under inert atmosphere

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from the UHV chamber into the electrochemical X-ray cell and contacted at open circuit potential in 0.1 M KOH. The experimental procedure followed that of similar experiments reported previously [4,5,12]. The crystal was indexed to a conventional hexagonal unit cell for the *fcc* (111) surface. The outer chamber of the X-ray cell was continuously purged with nitrogen to protect the Ag surface from oxygen. The reference electrode was a saturated calomel electrode (SCE) and all potentials are quoted versus this reference.

3. Results and discussion

The cyclic voltammetry of Ag(111) in 0.1 M KOH is shown in Fig. 1 (a). The broad reversible feature observable in the cyclic voltammetry between ~−0.8 V and −0.4 V can been assigned to the adsorption of

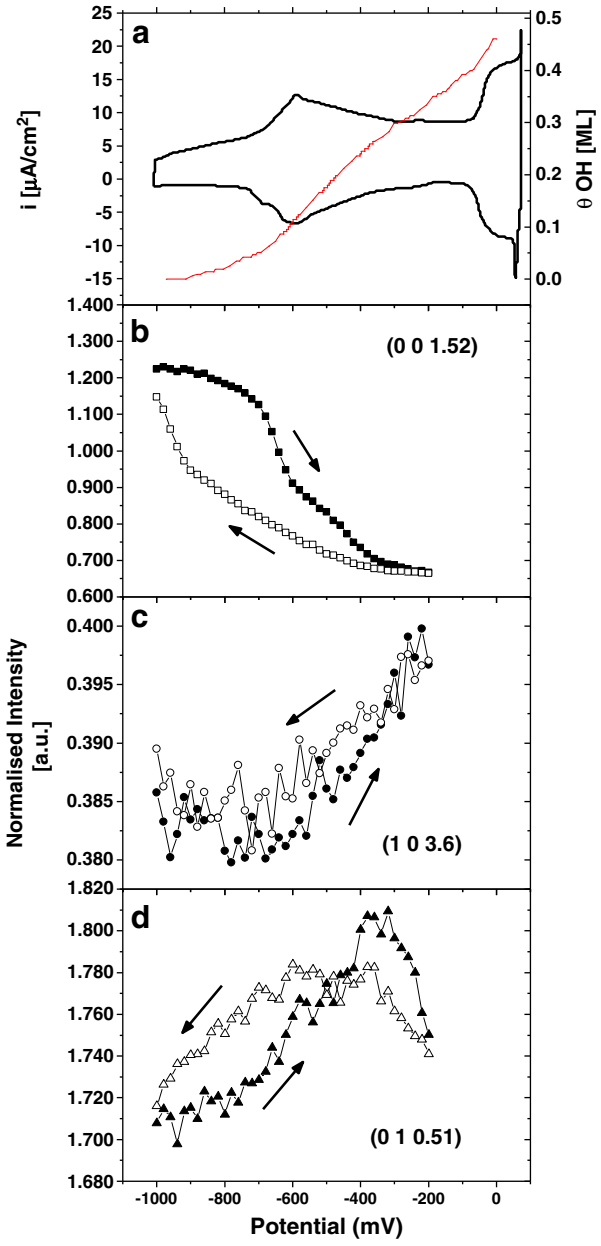

Fig. 1. (a) Cyclic voltammetry of Ag(111) in 0.1 M KOH recorded at a sweep rate of 50 mV/s, the potential dependent coverage by OH_{ad} calculated from the CV is shown as a solid red line. X-ray voltammetry (XRV) measured at (b) (0, 0, 1.52), (c) (1, 0, 3.6) and (d) (0, 1, 0.51). The sweep rate for the XRV measurements was 5 mV/s.

OH^- anions in agreement with various in-situ and classical electrochemical measurements [8–11,13]. Based on a 1-electron transfer the OH coverage can be calculated from the charge under the CV (dash–dot line) and shows a gradual increase in θ_{OH}, following the classic shape common for specific adsorption of anions on metal surfaces. The adsorption of OH^- is a precursor to the formation of an Ag_2O surface oxide phase at potentials > −0.1 V [14].

X-ray voltammetry (XRV) measurements [5,12], in which the scattered X-ray intensity at structure-sensitive reciprocal lattice positions is measured as a function of the applied electrode potential, were made and representative results (background subtracted) are shown in Fig. 1; (b) at (0, 0, 1.52), an 'anti-Bragg' position on the specular CTR sensitive to any layered ordering at the interface, (c) (1, 0, 3.6), which is primarily sensitive to lattice relaxation of the Ag surface, and (d) (0, 1, 0.51), an 'anti-Bragg' position on the non-specular CTR which is sensitive to interfacial atomic positions that are commensurate with the Ag lattice. The fact that the changes at the non-specular CTR positions are very small (~4%) indicates that there are only subtle changes to the Ag surface. In contrast, the changes at the specular CTR position are relatively large (~50% change in scattered intensity). As the intensity along the specular CTR is sensitive to ordering normal to the interface, including species that are not necessarily commensurate with the Ag lattice, this implies that there are significant structural changes on the electrolyte side of the interface.

In order to derive a structural model for the interface, CTR data at fixed potentials (−1.0 V and −0.2 V) were measured by performing rocking scans around the surface normal at successive L values to obtain background-subtracted integrated intensities. The error bars correspond to the statistical error from the measurements combined with an estimated 5% systematic error. Fig. 2(a,b) shows the specular, (0, 0, L), and non-specular, (1, 0, L), CTR data measured at E = −1.0 V (circles) and −0.2 V (squares). This potential corresponds to the double layer region and no species are chemically bonded to the surface. The best fits to the CTR data (solid line) were obtained using a least-squares method in which the variable structural parameters were the surface atomic layer expansion and the *rms* surface roughness (σ_{Ag}). At −1.0 V the best fit indicates that the surface Ag layer has a slightly reduced occupancy ($\theta = 0.94$), undergoes a small *inward* relaxation of ~0.7% of the Ag(111) layer spacing ($d_{(111)} = 2.36$ Å) and $\sigma = 0.07 \pm 0.03$ Å (modeled using a static Debye–Waller factor). This structural model gives a good fit to the (1, 0, L) CTR data but does not give a good fit to the specular CTR (calculated dashed line). In order to get a good fit to the specular CTR data it was necessary to incorporate layering in the electrolyte side of the interface. In modeling the interface structure a contribution from the bulk electrolyte, represented by an error function going from zero to infinity in the surface normal direction and saturating at the bulk density of water at a distance of ~7 Å from the interface was included [6,14]. In order to get a good fit to the specular CTR data (solid line) it was necessary to include a layer in the electrolyte at a distance of 4.1 Å from the topmost Ag layer. Given that there is no specific adsorption at negative electrode potentials, we assign this layer to hydrated K^+ cations in the outer part of the double layer. The best fit to the data has a cation layer with a surface coverage, $\theta_{K+} = 0.25 \pm 0.1$ ML at a distance, $d_{Ag-K+} = 4.1 \pm 0.3$ Å above the Ag surface and $\sigma = 0.25 \pm 0.1$ Å. The incorporation of the cation layer in the model substantially improves the reduced χ^2 value for the fit from $\chi^2 = 2.8$ to $\chi^2 = 1.3$.

As shown by the XRV data in Fig. 1, scanning the electrode potential from −1.0 V to −0.2 V substantially changes the specular CTR data. CTR data were measured at −0.2 V and a ratio of the 2 CTR data sets ($R = I_{-0.2V}/I_{-1.0V}$) is plotted in Fig. 2(c,d). Clear systematic changes in the CTR data are highlighted by the ratio data set which is consistent with the potentiodynamic measurements presented in Fig. 1. The non-specular CTR ratio data can be modeled by a change of relaxation at the Ag surface. The solid lines are a best fit to the