Structural Kinetics of Halide Electroadsorption

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Introduction

Structural information on halide electroadsorption has been obtained both with surface x-ray scattering and scanning tunneling microscopy for Cl^-, Br^-, and I^- adsorption on the (111), (100) and (110) facets of Au.[1] These studies have demonstrated that a variety of ordered phases, both commensurate and incommensurate, can form. Previously, kinetic studies of electrode surface phase transitions were not possible on millisecond time scales because of the thin electrolyte layer used in conventional x-ray cells. Although the 10-20 μm solution layer reduces the x-ray adsorpion, it yields a large, nonuniform RC time constant. For instance, with concentrated solutions, the the cell time constant maybe as fast as 10 msec near the edge of the crystal but is typically only 1000 msec at the center of a 1-cm-diameter crystal. Here we report kinetic studies of Br electroadsorption on Au(100) obtained in an x-ray cell with a uniform 1 msec time constant. This three order of magnitude increase in the cell time constant was achieved using a windowless, electyrolyte "drop cell."

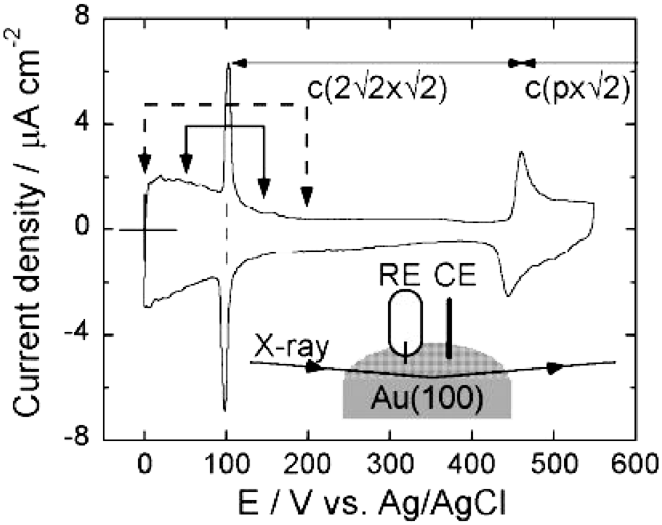

FIG. 1. Voltametry curve of Au(100) in 0.1 M HClO4 containing 10 mM KBr.

Methods and Materials

The drop cell is illustrated in the inset of Fig. 1, where a drop of electrolyte covers the single crystal electrode surface and the reference (RE) and counter electrodes (CE) are placed from above in close proximity to the surface. Measurements were performed using the CMC liquid spectrometer, which kept the sample horizontal while accessing reciprocal space. The energy of the x-ray beam was 18.5 keV, which significantly reduced the loss of intensity in passing through the solution drop and the amount of radiation-generated hydrogen peroxide (which affects the adosrption measurements) as compared to the 8-10 keV x-ray beam commonly used.

Results and Discussion

Figure 1 shows the voltametry curve for bromide adsorption on Au(100) where two pairs of current peaks separate three different bromide adlayer phases. Measurements of the phase transformation kinetics between the disordered and the commensurate c(√2×2√2) phases were carried out by cycling the potential (8 Hz using a square wave) between potentials 100 or 50 mV positive and negative of the critical potential, E_c. The x-ray intensity at a super lattice position were collected for 1000 cycles using a multichannel scaler (MCS) with a dwell time of 0.1 msec.

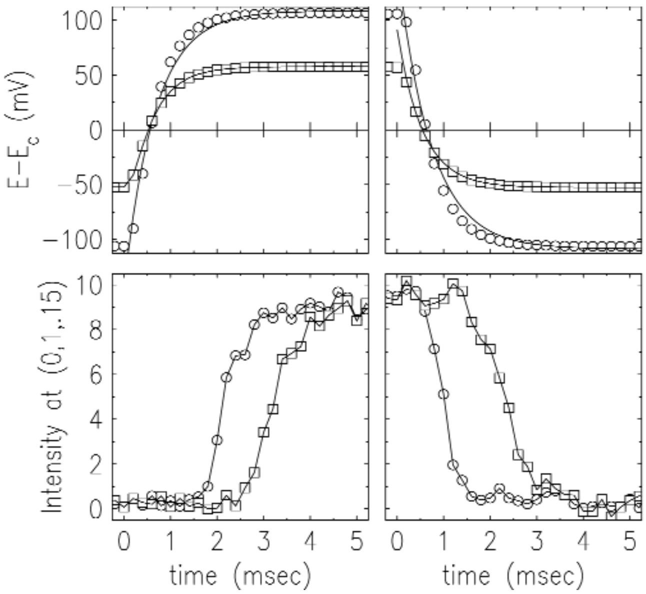

FIG. 2. Time dependences of potential (top) and x-ray intensity (bottom) in ordering (left) and disordering (right) process.

As shown in Fig. 2, the disordering (decreasing intensity upon a negative potential step) is faster than the ordering process (increasing intensity upon a positive potential step). Both processes are slower with smaller overpotentials ($E-E_c = \pm 50$ mV compared to $E-E_c = \pm 100$ mV), while the time constants for all the potential steps are essentially the same, with the exponential RC time constant less than 1 msec.

Acknowldgment

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References

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