

Formation and Diffusion of Subsurface Adsorbates at Electrodes

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Supporting Information

Experimental procedures

For the experiments a home-built electrochemical video-STM was used, which is described in Ref. 1. The Ag(100) single crystal samples (Mateck) were prepared by chemical polishing with cyanide, described in Ref. 2, followed by annealing at approximately 750 °C in an induction oven under Ar atmosphere. Subsequently, the samples were first immersed in 1 mM HClO₄ or NaClO₄ solution, prepared from suprapure perchloric acid (Merck), p.a. NaClO₄ (Sigma Aldrich), and ultrapure water. In this solution, potential control versus an Ag/AgCl (sat.) reference electrode was established, which was calibrated with respect to a Standard Calomel Electrode (SCE) before and after the measurements. Then, the solution was continuously exchanged to 1 mM HClO₄ + 1 mM KBr (Merck, p.a.) solution (pH 3) or pure 1 mM KBr solution (pH 7), respectively, while keeping the potential in the double layer potential regime. Dosing of the sulfide adsorbate on the Ag surface was performed using the same procedure successfully employed in our previous Video-STM studies of sulfide diffusion,^{3,4} i.e., by adding 3 to 10 µl of a 5 to 10 µM Na₂S (Alfa Aesar, p.a.) solution to the STM cell. After waiting times of ≥ 45 min. to allow for full adsorption of the sulfide in the solution, this resulted in sulfide surface coverages in the low percentage regime. Subsequently, the *in situ* STM experiments commenced. Video sequences were recorded in constant height mode at image acquisition rates of 10 images per second, using polypropylene-covered tungsten tips. A fixed tunneling bias of 100 mV and currents of 1 to 10 nA were used. The data were obtained at room temperature in the potential range -0.27 to -0.04 V_{SCE}, which is clearly negative of the onset of AgBr formation in the employed electrolytes (see Figure 1SI). At more negative potentials than -0.27 V, the sulfide surface mobility becomes too high for Video-STM studies. At all employed potentials, the Ag(100) surface is fully covered by a c(2×2)-Br adlayer, which is present on the surface down to -0.7 V.^{5,6} The pseudo-capacitive current peaks, caused by Br adsorption/desorption and c(2×2)-Br disordering,⁵ are masked by the hydrogen evolution current in our electrolyte solutions.

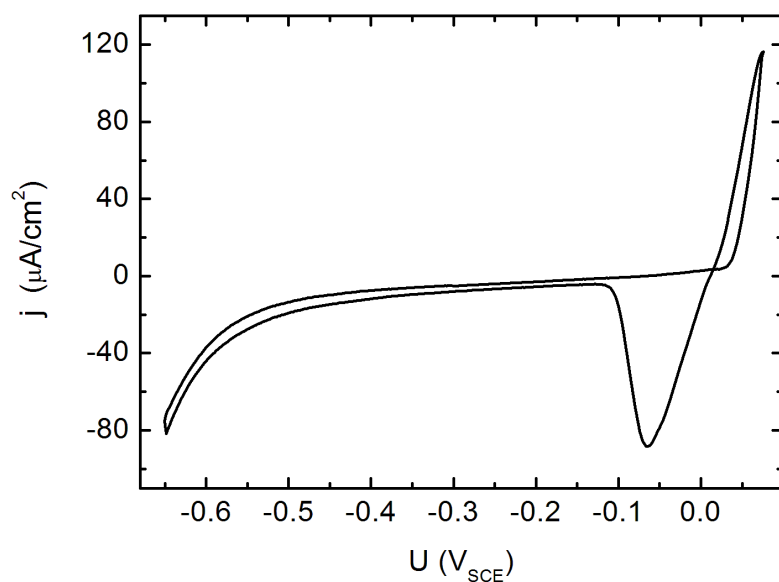


Figure 1SI. Cyclic voltammogram of Ag(100) in 1 mM HClO₄ + 1 mM KBr, obtained at a sweep rate of 25 mV/s. The double layer region extends from -0.55 to +0.04 V and is limited at the upper end by the onset of bulk AgBr formation.

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