Time Response of Br on Ag(100) in Electrochemical Thin Layer Geometry

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We studied the thin layer time response of Br adlayer on a Ag(100) electrode. As the electric potential is varied a second order phase transition occurs at approximately –0.72 V. The time response of the cell was experimentally observed and compared with theoretical predictions.

We prepared an electrochemical cell of Ag(100) in a thin layer of $NaClO_4$ and KBr solution (pH ~10). Surface X-ray scattering reveals a Bragg rod at (½, ½, L) for potentials above approximately –0.72V when the body-centered tetragonal unit cell is used. Below this potential the peak vanishes (**Figure 1**).

X-ray scattering in the (1, 0, L) direction revealed a smooth decrease in intensity as the potential increased. The absence of a sharp transition in this direction suggests that the sudden appearance of a Bragg rod in the (½, ½, L) direction is not due to a sudden change in coverage. Rather the Bragg rod appears because of a second order phase transition in which the surface layer changes from a disordered lattice gas into an ordered c(2x2) phase. Such a phase transition would not be observed in the (1, 0, L) direction.

We measured the time response of the x-ray signal using a stand alone multi-channel scaler (MCS) which allowed us to measure the time response at a fixed position by averaging over many potential cycles. A square wave potential with a period of 0.47 sec was applied to the electrode which periodically switched the potential between the ordered and disordered potential regimes. To collect the data, we set the bin size of the MCS to 0.4 msec and the data was collected in 1024 channels (~0.4 sec). A typical data set is shown in **Figure 2** in which data was collected for 500 cycles. The rise and fall of the intensity corresponds to the rise and fall of the potential cycle.

We modeled the thin layer electrochemical cell as a RC circuit and determined the theoretical time response of the potential inside the cell due to the applied step potential at the edge. The resulting potential was substituted into the curve of **Figure 1** to yield the theoretical time response intensity of the Bragg reflection in the (½, ½, L) direction (**Figure 2**).

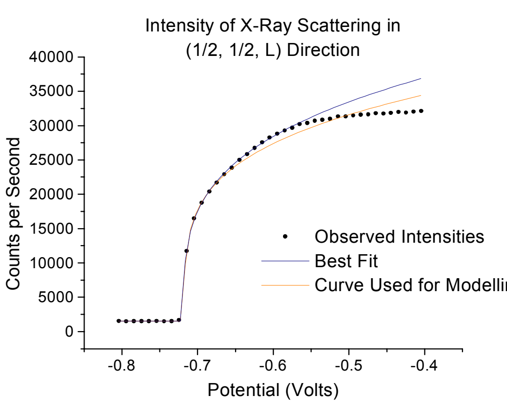

Figure 1. Relative intensity of scattering in (½, ½, L) direction (L=0.07). The curve is fit to a power law two times: The dark curve is the best fit. The light curve was used for determining the theoretical time response shown in figure 2.

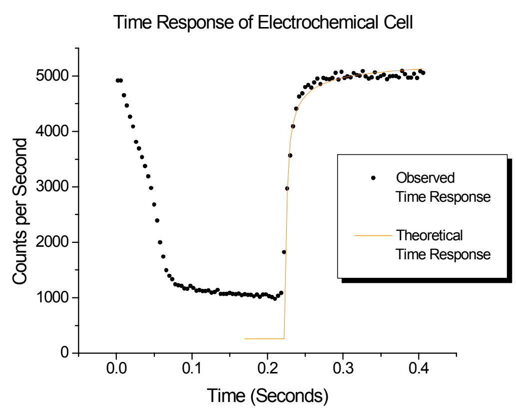

Figure 2. Observed time response in (½, ½, L) direction (L=0.07) as potential steps from -506 mV to -748 mV and back to -506 mV. The average count of each consecutive set of 10 channels is plotted. The curve represents the theoretical time response of the cell when modeled as RC circuit with time constant ~ 8000 s/m^2.