

Early stages of iron passivation: defective growth of oxide layer observed by quick X-ray reflectometry

Chemical reactions at solid-liquid interfaces are, although quite common in chemistry, one of the most challenging phenomena in condensed matter physics. Usually, chemical reactions are explained in terms of thermodynamic potential. To gain physical insight into such phenomena, the atomistic visualization of a reaction process is highly desirable. Passivation is one of the chemical reactions that can be controlled by applying external electric voltage. Here, we take iron passivation as a typical example of a chemical reaction at solid-liquid interfaces in our microscopic study.

A passive layer of iron is known to have a defective spinel structure. The typical time scale of iron passivation at the interface between iron and an aqueous solution is twofold: a few seconds and a few years. The slow process is well explained by the point defect model (PDM) [1,2], where the time evolution of the oxide layer thickness is $dL/dt = A \exp(-BL)$, with L , t , and A and B denoting the thickness, time, and two constants, respectively. In contrast, the fast process is not understood well, partially because of the difficulty in experimental observation as well as the variety of sources of time evolution. We performed time-resolved X-ray reflectivity measurements to elucidate the time evolution of the iron oxide film growing in a pH 8.4 borate buffer solution.

The typical time scale of X-ray reflectometry is a few minutes [2], which is very slow for the fast time scale of iron passivation. In this study, we used the stationary photography method for imperfect surfaces [3]. An imperfect surface produces a broad signal in the reciprocal space having a finite range of overlap with the Ewald sphere, as shown in the inset of

Fig. 1(b). This method allows us to measure reflectivity profiles without moving the diffractometer, and the time resolution of the measurement is only limited by the statistics. Using the strong undulator X-ray at SPing-8 BL13XU and the aid of Bayesian inference, we achieved a 20 ms time resolution [4] to obtain the reliable real space information of the iron oxide.

Iron single crystals were immersed in borate buffer solution. Their electric potential was controlled by a potentiostat using a Ag/AgCl reference electrode. The potential of -0.8 V versus Ag/AgCl makes the iron/buffer solution interface stable, while $+0.3$ to $+0.7$ V versus Ag/AgCl makes the passive surface stable. In reflectivity measurements, a 25 keV X-ray beam passes 10 mm into the solution. The absorption is less than half of the total intensity. The reflected beam was measured by a PILATUS detector with a 20 ms exposure time and a 5 ms interval. A typical signal obtained with 20 ms exposure is presented in Fig. 1(a). The blue curves show the 2000 samples obtained by Monte Carlo sampling for the Bayesian inference. Corresponding real-space electron densities ρ are presented in Fig. 1(b). The electron density shows four plateaus: iron, passive layer, outer layer, and buffer solution from left to right. The time evolution of the electron density and the thickness of the passive layer (ρ and L) was derived from a similar analysis of all the 20-ms-exposure photographs. The results are presented in Fig. 2. The dashed line for L shows the PDM prediction, and the experimental result deviates from it in the first 1 s of oxidation. The saturation value of ρ for the passive layer is close to the density of magnetite and greater than ρ at the

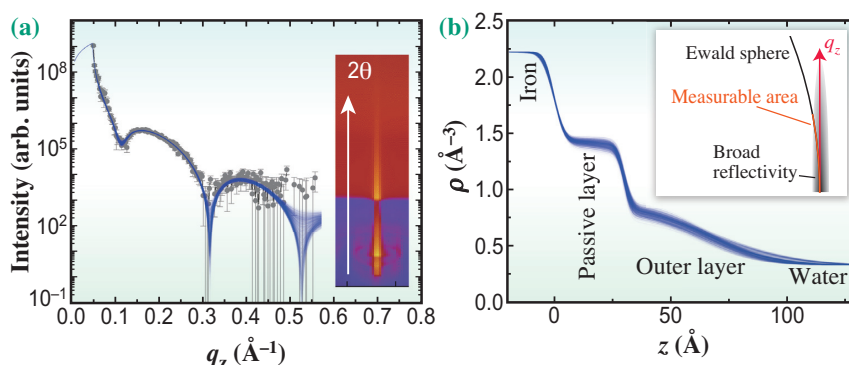


Fig. 1. (a) X-ray reflectivity profile measured with 20 ms exposure. Solid gray circles show the experimental result. The inset shows a PILATUS image. An attenuator was inserted in the low-scattering-angle region to improve the dynamic range. (b) Electron density profile around the iron surface derived from the reflectivity profile shown in (a). The inset shows a schematic of the broad reflectivity profile in reciprocal space from an imperfect surface. The Ewald sphere overlaps a finite area of the reflectivity profile along q_z . The blue curves for both panels show the 2000 samples obtained by Monte Carlo sampling. [4]

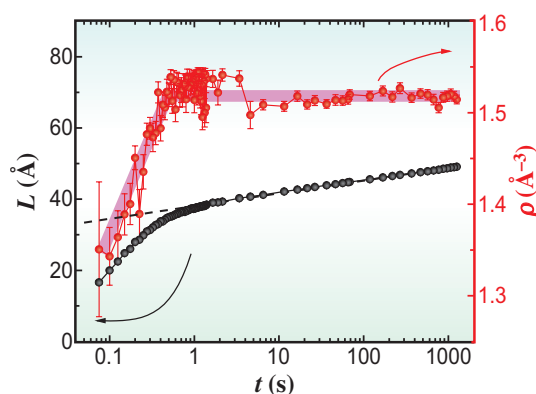


Fig. 2. Thickness L (black) and electron density ρ (red) of the passive layer grown at +0.7 V as a function of time t . Direct logarithmic law $L = \alpha \ln(t) + \beta$ (dashed line) is followed only when $t > 1$ s. The pink solid line is a guide for the eye. [4]

beginning of film growth, indicating that a passive film with many defects is formed at the first stage of passivation.

Different time evolutions of ρ and L in the first 1 s of the passivation process indicate a change in the rate-limiting process. Let us discuss the film growth process using a schematic of the potential profile presented in Fig. 3. In the framework of the PDM, there is a constant electric field, i.e., a constant slope in electric potential, inside the oxide film. The potential of the bulk solution and that of bulk iron are connected by the potential step at the two electric double layers formed at the metal-film and film-liquid interfaces as well as the potential slope in

the oxide film. When the film is thick, the potential discontinuities at the interfaces are small, as depicted in the inset of Fig. 3. This change causes an increase in potential barrier between the metal iron and oxide iron sites, as presented by the thick curves in Fig. 3. Therefore, when the film is very thin, the iron supply from the metal side to the oxide side should be rapid, and the rate limiting process should be the oxygen supply from the liquid-film interface. When the film becomes thicker, the barrier between the metal iron and the oxide iron sites is high, as depicted by the thick black curve. The rate-limiting process is then changed to the cation supply from the metal side to the oxide side.

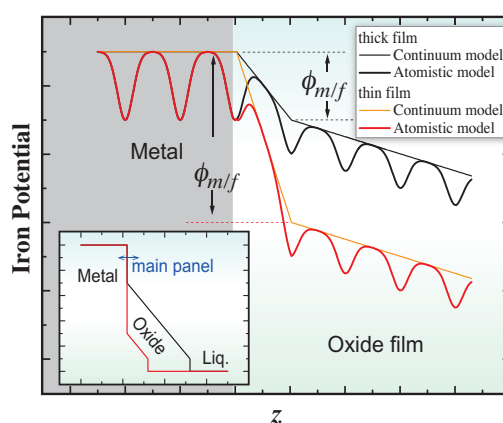


Fig. 3. Schematic of the iron potential profile around the metal-oxide interface. The thin curves show the profiles for the continuum approximation or ordinary PDM, and the thick curves show the profiles for the atomistic model. Black and red profiles are for thick and thin oxide films, respectively. $\phi_{m/f}$ denotes the potential difference between the metal and oxide regions. Inset: The potential curve for a wider z range. [4]

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References

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