***In situ* Monitoring of pH at the Electrode|Electrolyte Interface During the Anodic Dissolution of Iron in Acidic Solutions**

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The anodic dissolution of iron in H_2SO_4 and HNO_3 solutions was studied by using scanning electrochemical microscopy (SECM) with a Pt ultramicroelectrode modified with polyaniline and by *in situ* monitoring of pH at the electrode|electrolyte interface. In each acidic solution, pH at the interface changed periodically during the observed current oscillations of iron, indicating that the oscillatory mechanism had some connection with pH. During the oscillatory processes, there were two layers of the film on the surface of the iron electrode: a loose outer layer ($\text{Fe}(\text{OH})_2$ and the salt film) and a dense inner layer (Fe_3O_4). First, the outer layer was formed gradually, and then the inner layer was formed under the protection of the outer layer. With the back diffusion of H^+ , the outer layer was dissolved gradually, indicating that the outer layer was mainly the $\text{Fe}(\text{OH})_2$ film; however, the inner layer was broken immediately after the dissolution of the outer layer. The results showed that pH of the solution played a key role and that the anions played a minor role during the current oscillations. It was reasonable to deduce that the oscillations were mainly caused by a periodic formation and dissolution of the oxide film. Furthermore, the salt film played a minor role even though the acid concentrations were high.

Keywords: current oscillations; pH; oxide film; iron; acid.

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