

The Iron Dissolution Mechanism in Changing Times – From a Classical Quasi-homogeneous Surface Approach to an Atomistic Consideration

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The iron dissolution and passivation mechanism represents one of the basic corrosion reactions. The counter reaction is either the hydrogen evolution or the oxygen reduction dominating in strong acidic and neutral solutions, respectively. These counter reactions overlap at pH about 4. According to the Wagner-Traud theory, the corrosion potential and the corrosion rate of the iron mixed electrode is determined by the kinetics of the metal dissolution and the counter reaction. In acidic solutions, the iron dissolution and the hydrogen evolution are charge transfer controlled reactions, whereas at higher pH the oxygen reduction is mainly a transport controlled reaction.

It is well accepted that the dissolution and passivation processes of the iron group metals (iron, cobalt, and nickel) in acidic solutions follow complicated mechanisms involving different oxygen-containing adsorbed intermediates (cf. refs. 1-3 and the literature cited therein). It was experimentally found that the dissolution and passivation rate of iron group metals strongly depends on the electrode potential, the composition of the electrolyte, and the pH. On the basis of steady state and non-steady state potentiostatic transient measurements, a first approach of the iron dissolution mechanism in the active range was proposed by the Russian scientists Roiter, Kabanov and Frumkin et al. at the end of the thirties and in the forties. At the end of the fifties, the German group of Bonhoeffer and Heusler observed a different set of kinetic data. They suggested the so-called “catalytic” iron dissolution mechanism. The rate determining charge transfer controlled step was assumed to take place at active surface sites. Later in the beginning of the sixties, Bockris, Drazic, and Despic in the US studied intensively the iron dissolution mechanism in acidic solutions in the active range. They obtained kinetic data similar to those of the Russians and proposed the so-called “consecutive” iron dissolution mechanism. In that time, several other groups all over the world confirmed either the data for the catalytic or those for the consecutive iron dissolution mechanism. For more than a decade, these different mechanisms dominated the controversially scientific discussions. However, in that time the electrochemical kinetics was dealt only on the basis of a quasi-homogeneous surface approach of the electrode. The influences of the substrate substructure and the substrate surface inhomogeneities on the kinetics of electrochemical reaction were completely disregarded.

Therefore, in the middle of the sixties, Lorenz et al. in Germany started extensive investigations on this topic. They showed that both sets of experimental data can be measured depending on the density of dislocations of the substrate. Also, the transition from the catalytic to the consecutive iron dissolution mechanism and vice versa was performed changing the substrate surface structure. Cathodic measurements on iron and cobalt deposition supported the theoretical assumptions of the important role of surface inhomogeneities on the kinetics of electrochemical charge transfer controlled reactions.

The development of Electrochemical Impedance Spectroscopy (EIS) by Eppelboin, Morel, Takenouti, Keddam, Wiart et al. in France in the late sixties and seventies opened a new window to study interfacial phenomena and reactions influenced by adsorbates and the substrate surface structure. In particular, the iron dissolution mechanism was intensively studied by the groups of Eppelboin et al. and Lorenz et al. using EIS. As remarkable results, the French colleagues accepted the existence of a catalytic charge transfer step, and the Germans introduced the potential-dependent surface relaxation of kinks as reaction sites in the discussion of EIS

spectra.

At the same time, Heusler et al. in Germany started highly sophisticated investigations on the dissolution kinetics and morphology of well-defined iron single crystal faces. As a main result, the iron dissolution kinetics could be quantitatively correlated to the density of monatomic steps and kink sites at the iron surface. This stage represented the start of modern surface electrochemistry. Lorenz, Jüttner et al. also used low-index planes of iron single crystals for iron dissolution studies. Both German groups agreed to interpret the obtained data on the basis of an atomistic approach.

In the eighties, the development of different Scanning Probe Microscopy (SPM) techniques and their introduction as in situ SPM methods at solid/liquid interfaces opened a new window to investigate both the structure of electrochemical interfaces and interfacial reactions on an atomic level. Different undersaturation (underpotential, UPD) phenomena forming so-called Low-Dimensional Systems (LDSs) at surface inhomogeneities of foreign single crystal substrate surfaces could be quantitatively interpreted in terms of atomistic considerations using in situ SPM results. Consequently, the oxygen containing reaction intermediates in the iron dissolution and passivation mechanisms were recently reconsidered applying this LDS concept (4). Now, one gets a complete new insight on an atomic level into the iron dissolution and passivation mechanisms, the breakdown of passivity, and pitting corrosion processes.

References

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