HYDROGEN ENTRY INTO IRON IN THE PRESENCE OF SURFACE SELF-ASSEMBLED SILOXANE NANOLAYERS

Ludmila Maksaeva,1 Maxim Petrunin1 and Andrey Marshakov1

1 Institute of Physical Chemistry, Russian Academy of Sciences
31 Leninsky pr., 119991 Moscow, Russia

The cathodic reaction of H3O+ reduction may lead to electrolytic hydrogen into iron matrix, that causes considerable changing mechanical properties of metal and susceptibility of iron to corrosion destruction. The determination of factors effected on hydrogen entry into metals and development of manners of inhibition of hydrogen permeation is very important problem. Organic silanes (RnSi(OR')4-n) are adsorbed on metal surfaces with formation of self assembled layers bonded with surface hydroxide radicals. The change of deposition conditions and chemical nature of silanes allows to control thickness, structure and properties of these layers. The organosilicon (siloxane) layers can be used to inhibit the hydrogen entry into iron. In addition, in spite of the processes of hydrogen permeation into iron in electrolyte and soil have been studied in a detail, the influence of hydrogen entry into a metal in atmosphere have never been studied. Whereas this phenomenon may play important role in the atmospheric corrosion processes, especially in the presence of corrosion active components of environment. The goals of present work are to study the processes of hydrogen evolution and permeation into iron in wide range of potentials and electrolyte pH to investigate the effect of organosilicon layers on hydrogen entry into metal, and to consider the possibilities of participation of hydrogen entry in atmospheric corrosion processes.

In order to determine the effect of condition of surface (namely the presence of surface layers) on hydrogen permeation into iron we synthesized of thin organosilicon layers on iron surface. The processes of hydrogen permeation into iron in the presence of siloxane layers under cathodic polarization conditions were studied. It was shown the marked effect of siloxane layers on hydrogen entry into metal at potential range from -0.2 to -1.8 V (nhe) and pH from 2 to 10. The influence of chemical nature, structure, and thickness of layers on rate of hydrogen entry are studied. It was shown maximal effect in the case of layers with hydrophobic properties. Decrease of hydrogen permeation rate was observed both at potential of hydroxonium discharge and at potential of water reduce. Formation of layers Langmuir-Blodgett films (on the base of octyl-, gexodecyl- and octodecylcontaining silanes) on iron surface leads to considerably decreasing current of hydrogen permeation into metal at both regions of potentials. The correlations between surface hydrophobity providing by organosilicon layers and inhibition action are obtained.

It is known that presence of so-called hydrogenation promoters in electrolyte markedly increase hydrogen entry into iron. So the introduction of SCN- ions in chloride -containing electrolyte provides the increase of hydrogen entry rate by a factor of 2 (in dependance on concentration). We studied organosilicon layers effect on hydrogen entry into iron in the presence of SCN- in order to clarify mechanism of rodanide promoting action and participation of organosilicon layers in hydrogen entry processes. It was shown that in this case silane layers decrease hydrogen permeation current. Moreover formation of mostly hydrophobic layers (for instance octodecyl containing silane) provides decreasing hydrogen permeation current in 20 and in 150 times at pH 2 and 10. Mechanism of rodanide promoting action in organosilicon layers presence and ways of iron hydrogenation decrease were suggested.

The influence of change of surface charge (by introducing ionogenic groups into organic radicals) hydrogen permeation rate have been studied. It was established that formation of siloxane layers allows to control cathodic processes and hydrogen permeation into metal matrix. The possibilities of direct control and inhibition of hydrogen entry processes including in the presence of hydrogenation promoters are considered.

Recently it was found that hydrogen permeation into iron can occur under anodic dissolution of metal. We have studied the hydrogen entry under pitting corrosion of iron. It was established that pitting initiation causes the increase of hydrogen flow into metal. Siloxane layers can inhibit pitting corrosion. We studied the siloxane layers on inhibition of hydrogen entry at pitting corrosion. The influence of surface charge was determined.