Study of hydrogen/adsorption absorption on iron electrode by electrochemical impedance techniques.

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This work concerns the interaction between hydrogen and a metallic host in the cathodic potential region. It was motivated by the need for a better understanding of the hydrogen insertion mechanism in metals.

Cathodic protection of steel in sea water produces hydrogen. This hydrogen enters and diffuses into steel structure and this insertion creates some constraints and induces defects or cracks. This phenomenon is called hydrogen embrittlement. As a first step, in order to understand hydrogen insertion, we studied the interaction between iron and hydrogen. For that, we elaborated electrochemical deposit with various thicknesses and we characterized these deposits by impedance measurements.

The experimental approach was inspired by the results of electrochemical measurements recently obtained for the hydrogen/palladium system[1, 2].

The processes occurring at the surface and within the iron films were studied using various electrochemical techniques. The impedance and voltametric behaviour was strongly dependant on film thickness.

Iron is in contact with an acid solution. In the cathodic potential range, the proton H^+ is supposed to be reduced on the iron surface in a way that an adsorbed hydrogen MH_{ads} is formed (Volmer reaction). Then, two reactions can occur: adsorbed hydrogen forms molecular hydrogen with another adsorbed hydrogen (Tafel reaction) or with a proton H^+ (Heyrvosky reaction), either hydrogen enters the iron and diffuses. So, hydrogen insertion and hydrogen evolution as bubbles coexist in the cathodic potential range.

To study interface phenomena, electrolytic iron were deposited on a gold electrode in order to stop hydrogen entry. For impedance measurements, an impinging jet cell[2] where the electrode surface was vertical, was used to eliminate bubbles with a 0.1 M sulfuric acid solution.

Figure 1 shows the impedance measured for various thicknesses of the iron layer at –1.1 V/ESS and figure 2 shows the variation of the charge transfer resistance for various thicknesses of the iron layer at –1,1 V/ESS and –1.2 V/ESS. Impedance diagrams of electrolytic iron show a semi circular capacitive loop like impedance diagrams of massive iron. But, we can see that the transfer resistance depends on the thickness of the iron film. Transfer resistance increases with the film thickness. This behavior is surprising as this term usually characterizes surface interactions so it should not vary with the thickness of the sample.

The hydrogen insertion behaviour in iron differed from that in palladium ; thus, the palladium model available in the literature can not be applied directly to iron.

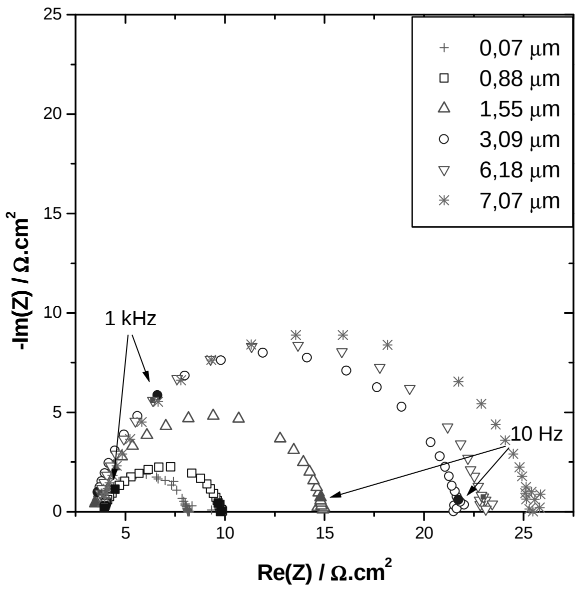

Figure 1 : Impedance diagrams of iron film on a gold electrode after stabilisation of the potential at –1,1 V/ESS.

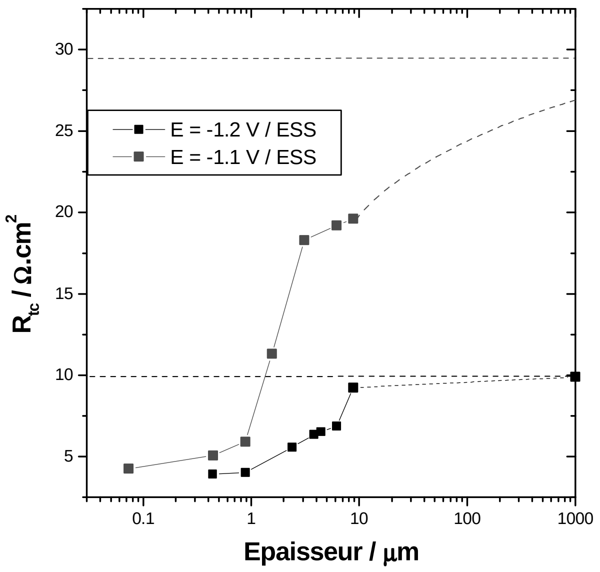

Figure 2 : Transfer resistance variation with the thickness of the iron film at different potentials. The horizontal dashed lines indicate the values of the transfer resistance measured on a very thick electrode.

References

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