Zn-Fe anomalous electrodeposition from sulfate electrolytes

S. L. Díaz[1], O. R. Mattos[1], O. E. Barcia[1,2]
1. Laboratório de Corrosão Prof. Manoel de Castro,
EE/PEMM/COPPE/UFRJ, Cx. Postal 68505,
CEP 21941-972, Rio de Janeiro, Brazil.
2. Dep. Físico-Química, IQ/UFRJ, Rio de Janeiro, Brazil.

The electrodeposition of Zn with Fe-group metals is classified as anomalous, since Zn deposits preferentially in most plating conditions. Although this phenomenon has been notorious, its mechanism remains not well elucidated. Among the hypothesis found in literature to explain this anomaly (1, 2) the most wide spread one suggests that the precipitation of $Zn(OH)_2$ at the cathode inhibits Fe deposition, due to a local pH increase (2).

The kinetics of ZnFe codeposition was investigated in acid sulfate solutions by interfacial pH (3, 4) and impedance measurements. In Fig. 1 it is shown the interfacial pH and current behaviors during individual Fe and Zn electrodeposition as well as during codeposition (75.5% Fe^{++} solution) at bulk pH=3.0. For the three systems, an interface alkalination is evident at the region in which hydrogen reaction prevails, i.e., at the non-linear part of polarization curves. The subsequent decrease in the interfacial pH is caused by the drop in the H^+ current. In the case of ZnFe system this decrease could also be associated with the establishment of the anomalous codeposition process, since Zn deposition begins to prevail (Fe content in the alloy < 75.5%). However, when metallic deposition becomes the main process, i.e., at the linear part of the curves, the interfacial pH reflects the predominant cathodic process. It can be observed in Fig. 1 that the interfacial pH increases during separate Fe deposition, meaning that it occurs with some kind of simultaneous consumption of H^+. On the contrary, individual Zn deposition brings about an H^+ inhibition. Accordingly, in Fig. 1, the prevailing of Zn deposition at the beginning of the linear branch of ZnFe curves results in an interfacial pH decrease. The observed rise on the interfacial pH at higher polarizations is a consequence of the Fe deposition control resume in both solutions. From this point on, the local pH clearly follows the increase of Fe content in the alloy. This suggests that the prevailing cathodic reaction governs the interfacial pH behavior. Therefore, the anomalous codeposition process does not seem to be associated with a saturation of any thermodynamic species at the electrode surface. It can only be described by kinetic arguments (4).

The impedance measurements corroborate these findings. In Fig. 2 it is shown the impedance diagrams obtained at the non-linear part of the polarization curves. Since in this region the H^+ reduction prevails, one can observe that the diagrams reflect this process, although metal deposition occurs with very poor current efficiency. In fact, the diagrams are very similar despite the presence of any of the metal ions. On the other hand, at the region where a current drop is observed, only the diagrams for Zn and ZnFe present a similar behavior, as seen in Fig. 3. This may indicate that a similar kind of blocking effect on hydrogen and Fe occurs and could be associated with a Zn containing species (4). At the very beginning of the linear part of the polarization curves, metal deposition begins to occur at high efficiency. It can be notice in Fig. 3 that, at this region, the diagrams reflect the corresponding deposition mechanism for the individual Fe and Zn (5). For ZnFe codeposition, the diagram shows a big inductive loop that could be related to the presence of a particular Zn rich phase.

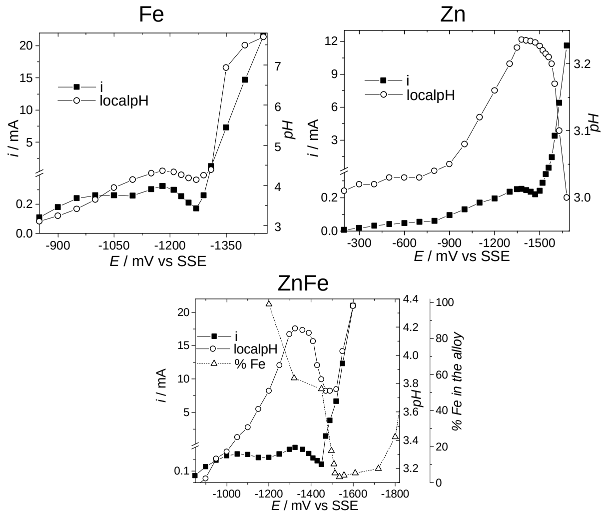

Fig. 1: Potential dependency of interfacial pH and current of individual Fe and Zn as well as of 75.5%Fe^{++} solutions.

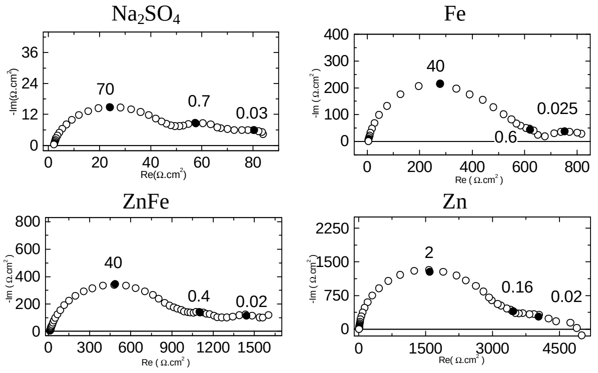

Fig. 2: Impedance measurements at the non-linear part of polarization curves for Fe, Zn, 75.5% Fe^{++} solution as well as for the solution without metal ions. (freq. in Hz).

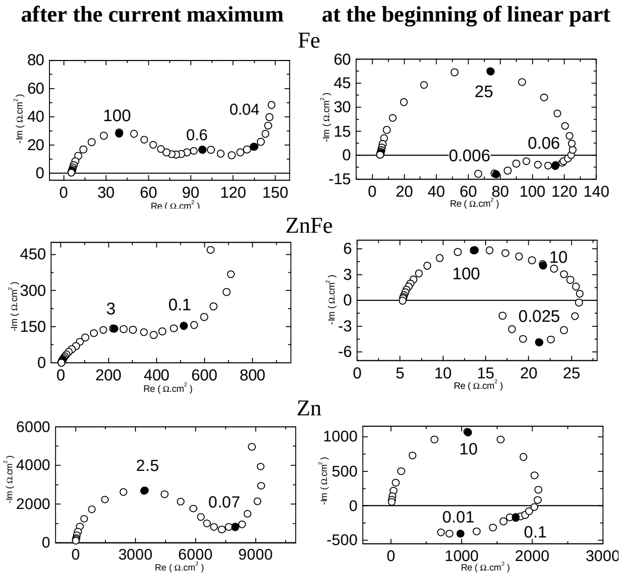

Fig. 3: Impedance measurements at the regions indicated for Fe, Zn and 75.5% Fe^{++} alloy solutions (freq. in Hz).

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