

RELATIONSHIP BETWEEN ZINC CORROSION PROCESS AND CORROSION PRODUCTS: AN EIS AND RAMAN SPECTROSCOPY STUDY

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Anodic dissolution of zinc has been widely studied in various corrosive media (1). In aerated low acidic sulfate solution, a three-path model (Fig. 1) applies satisfactorily when considering low dissolution current densities (2), and for various zinc coatings (3).

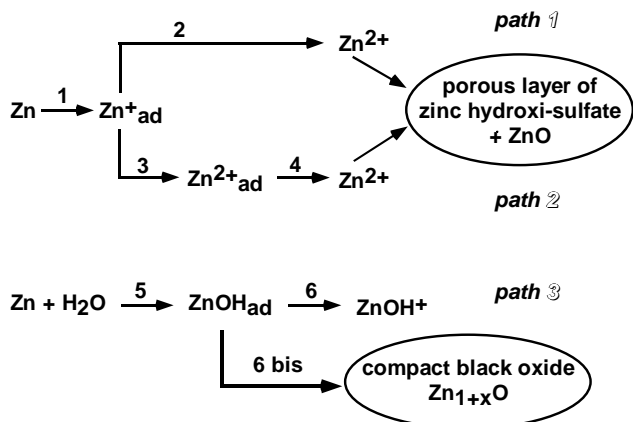


Figure 1: 3-path reaction model accounting for zinc dissolution in low acidic medium.

A detailed examination of pure zinc corrosion processes was performed by *in situ* Electrochemical Impedance Spectroscopy, and a product characterization by Raman Spectroscopy. In a 0.5 mol.L⁻¹ Na₂SO₄ solution, the corrosion layer exhibits a duplex structure as reported in Fig. 2. The upper layer composition was identified to be a mixed zinc hydroxi-sulfate and zinc oxide ZnO products (Fig. 3a). The Raman analysis of the whole crust of corrosion products (Fig. 3b) exhibits an additional vibration mode at *ca* 570 cm⁻¹ that was ascribed to a non-stoichiometric zinc oxide Zn_{1+x}O (Fig. 3c & 3d). It is preferentially formed in close contact with zinc, forming a compact black corrosion layer.

Such a similar duplex structure was already reported in the case of zinc oxidation in strong alkaline decarbonated media, the upper layer being ZnO (4).

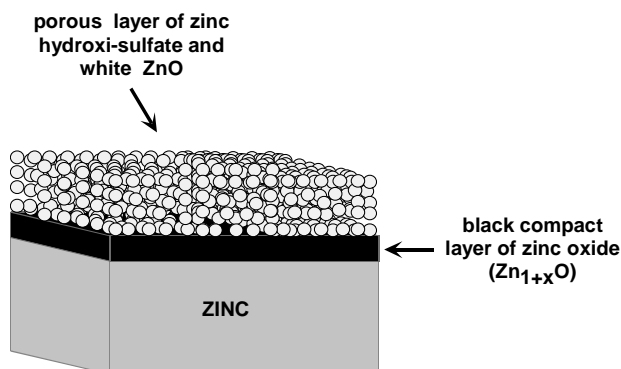


Figure 2: Schematic view of zinc oxidation products stacking.

The study of various zinc coatings (hot dip zinc or electrodeposited zinc from acidic or alkaline media) evidenced in all cases the presence of a bi-layer structure. We show that there is a strong correlation between the two kinds of corrosion products and the dissolution model. The black oxide is formed through path 3 from the Zn(OH)_{ads} intermediate, whereas crystals of zinc hydroxi-sulfates are produced by a precipitation mechanism involving the Zn²⁺ ions formed by paths 1 and 2. When time is elapsing, the thicknesses of the layers are increasing. EIS measurements evidenced that:

- In addition to the double layer capacitance, the black oxide layer introduces a capacitive term which can be ascribed to the semi-conducting character of this material.
- The porous zinc hydroxi-sulfates layer introduces a diffusion term in the high frequency range of the impedance that significantly flattened the charge transfer loop.

The latest was confirmed using calculations for a porous electrode with the De Levie model (5).

We also put in evidence that the anodic behavior of zinc in low acidic chloride media (0.5 mol.L⁻¹ NaCl) can be described with the same model and leads as well, to the formation of two layers of corrosion products the upper being a zinc hydroxi-chloride.

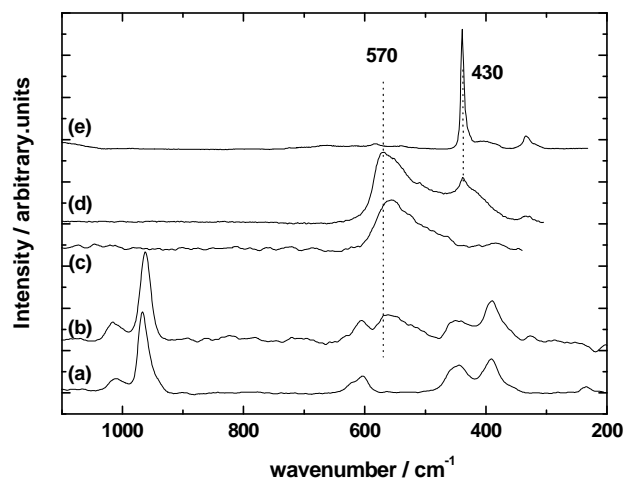


Figure 3: Raman spectra of zinc corrosion products: a) spectrum of the upper part layer: (Zinc hydroxi-sulfate); b) spectrum of the whole corrosion layer; c) spectrum of the black oxide layer: Zn_{1+x}O; d) spectrum given by a ZnO crystal lying on the black oxide layer; e) ZnO reference spectrum (Wurtzite structure)

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