

Behavior of Thin layers of Green Rusts electrochemically deposited on iron and inert substrates.

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The corrosion of iron is a well-known problem in many domains like environment, nuclear, ... Even if anti-corrosion solutions exist, it is practically impossible to avoid the formation of oxidation products, especially in the case of long-time contact of iron with corrosive media.

The formation and structure of corrosion layers are often very complex because a variety of corrosion products can be formed, depending essentially on the species present in the medium (soil, water, ...). Understanding the transformation pathways that occur during the growth and evolution of a corrosion layer is a hard challenge since it is difficult to clearly identify the contributions of each corrosion product and the influence of the iron substrate. Moreover, intermediate compounds like green rusts [1] or amorphous ferric phases, are particularly reactive and could induce local modifications that can result from redox or adsorption reactions with species present in the corrosive media.

That is why the studies on the behavior of an oxidation product formed alone dependently and independently of iron or another compound are very interesting for many applications. In this case, it is possible to get a better understanding of the transformation or the stability of the compound and the relationships with its local environment (oxidant or reductive media), with the presence of inhibiting species like silicate or phosphate ions, ... Moreover the interactivity of the product can be studied when it is in contact with very redox-active species like chromate, actinides, ... [2].

In this way, we studied the electrochemical synthesis of thin layers of iron corrosion products on iron and inert substrates (Au, Pt). Common corrosion products (goethite, siderite, magnetite, ...) could be formed following this way of synthesis, as well as some intermediate products such as green rusts (GR1 and GR2), amorphous ferric phases, ... In the case of green rusts and as far as we know, it is the first time that the synthesis of such thin layers has been reported on an inert substrate.

Studying the corrosion product as a thin layer on a conducting substrate has many advantages compared to a powder or a suspension : (i) the manipulation of samples and their treatment (rinsing, drying) is generally easier, (ii) electrochemical measurements can be directly performed and coupled to in-situ techniques such as electrochemical quartz microbalance (EQCM), micro-Raman spectroscopy, (iii) ex-situ analyses (SEM, XPS, IRRAS) are more easily operated even if the amount of product is low.

This presentation will be particularly focussed on the synthesis of thin layers of green rusts incorporating anions such as carbonate or chloride (GRs1) or sulphate (GR2) on iron, platinum or gold substrates, and on their electrochemical behavior. These compounds belong to the layered double hydroxides (LDH) group and have the general formula $Fe^{II}_{(1-x)}Fe^{III}_x(OH)_2 \cdot [x/nA^{n-}, mH_2O]$. They are intermediate products that may play an important role during the building and evolution of corrosion layers. The

influence of parameters like concentration, pH temperature or potential on the synthesis will be detailed, as well as the characterization of the films by means of usual techniques such as FTIR, XRD, SEM, EDS ... Figure 1 gives the SEM image of a carbonate green rust layer, showing large well-crystallized particles. Figure 2 illustrates the kind of information that can be obtained from a voltammetric study performed with a carbonate green rust (GRc) layer in contact with a solution of hydrogenocarbonate. The GRc-into-Fe(III)* solid-state oxidation is revealed by the anodic peak ; two cathodic peaks are observed on the reverse scan due to the progressive transformation of Fe(III)* into Fe(III) [3]. Such electrochemical measurements give information on the behavior of green rusts and on the transformation pathways involving these species.

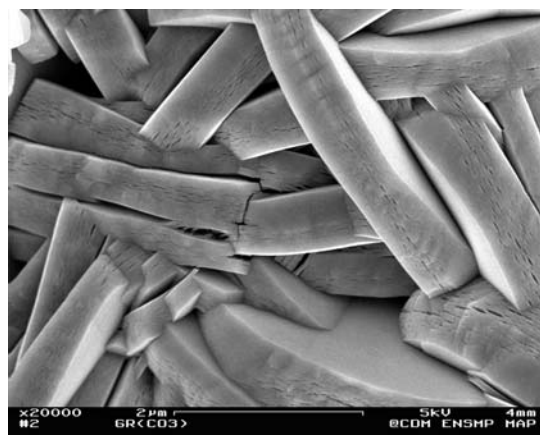


Figure 1: Thin layer of green rust deposited on gold.

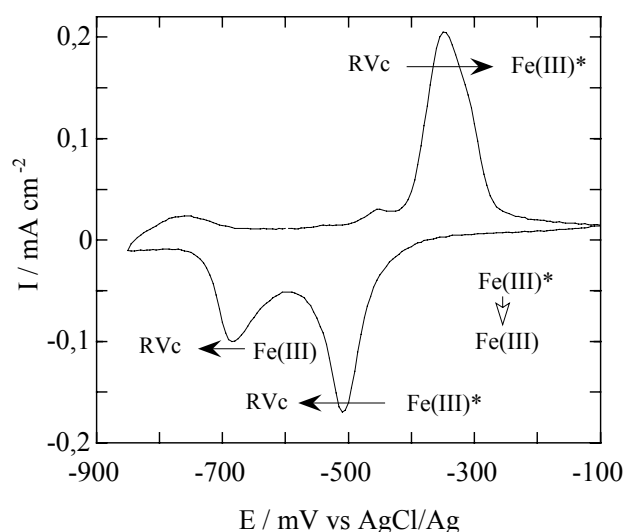


Figure 2: Voltammogram of thin layer of green rust deposited on iron in contact with a solution presented the characteristics : $[NaHCO_3] = 0.4 M$; $pH = 9.6$; $25^\circ C$.

References :

- [1] R. M. Taylor, Clay Miner. **15**, (1980) 369.
- [2] G. B. W. Aaron, M.M. Scherer, Environ. Sci. Technol. **35** (2001) 17.
- [3] L. Legrand, R. Maksoub, G. Sagon, S. Lecomte, A. Chausse, J. Electrochem. Soc. In press.