

## Composite Oxide/CP or Large Size Anions/CP Films as Active Protective Coatings. Case of Polypyrrole.

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Conductive Polymers (CP) have been widely investigated recently as substitute materials for primers in protective coatings. The mechanisms involved are either a barrier effect towards corrosive species or anodic protection in the case of metals having a passivity domain.

Among the different envisaged substrates, iron, carbon steel, Al, Mg, Cu, Zn have been tested with either Polyaniline or Polypyrrole (Ppy).

In a previous work, the protection mechanism against corrosion and its breakdown in a concentrated chloride solution for an oxalate doped Ppy coated iron has been established [1]. The first step in the open circuit potential measurements was the existence of a potential plateau in the passivity domain which corresponded to the equilibration of the film during the exchange of oxalate and chloride ions. The end of the first plateau was characterized by a significant jump of the potential and corresponded to the contact of chloride ions with the passive film and the first occurrence of pitting. A second step was analyzed as corresponding to an alternation of pitting and healing of the passive layer, related either to the oxidizing abilities of the passive layer or to the precipitation of a protective -but not passive- film of iron oxalate.

The third and last step marked by a return of the potential to the normal corrosion potential of iron, indicated that the film was unable to re-oxidize the metal till the passivity domain.

In this sequence of events, the most critical one was the ingress in the Ppy film and propagation of chloride ions towards the passive film. EIS measurements confirm this interpretation and showed in addition that the diagrams were only characteristic of the Ppy film, allowing one to follow the evolution of the film doping.

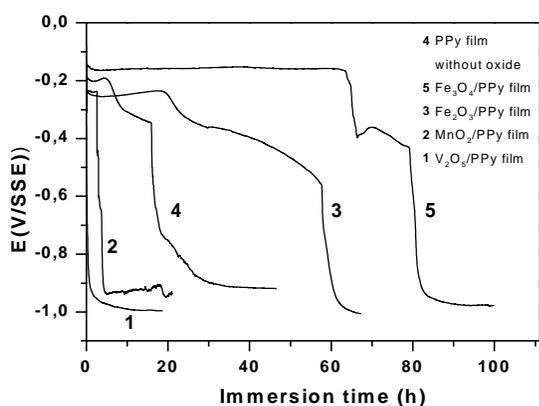


Figure 1 : Time evolution of the Open circuit potential for Ppy/oxalate/oxide composite films electrosynthesized on iron electrodes. Test medium : 3% NaCl solution. The synthesis charge for all films was  $2C.cm^{-2}$  corresponding to an average thickness of  $3\mu m$ .

So as to improve the protective performances of the CP film, two routes have been explored : The first one was to

increase the oxidizing abilities of the film. This goal was achieved by synthesizing composite films with the CP as matrix and oxide particles as load [2]. Different oxides has been tested. Among them  $Fe_3O_4$  gives the best results (Fig1).

The second one presented in this work was to modify the selective properties of the Ppy film so as to prevent or at least severely restrict the ingress of chloride ions in the film. This was achieved by changing the permselectivity of Ppy from anionic to cationic.

To this end, different anions of large size have been tested. For such a system, the anion which is the counterion for the synthesis is trapped in the matrix and cannot be exchanged in doping-dedoping sequences. In this case, and after synthesis completion, the cations (co-ions) only can be exchanged and therefore the penetration of chloride ions is strongly reduced.

However, the parameters controlling the insertion of oxide particles is quite complex and not all parameters controlling this process are yet handled: particle sizes, density, surface charge, and the hydrodynamic parameters.

Different large size anions have been tested, among which Polystyrenesulfonate (PSS) or Sodium dodecylsulfate (SDS). In this case, the coating is a duplex film, where the inner film is synthesized in the presence of oxalate only because either of these large size counter-ions are unable to achieve a satisfactory passive layer. The results in Fig. 2 clearly indicate that SDS provides a much better protective efficiency but for the investigated synthesis conditions, one observes that a marked optimum is obtained for a relatively low synthesis charge. This might be due to increasing mechanical constraints with increasing film thickness.

The performances of these different systems will be discussed on the basis of OCP and EIS quantitative analysis.

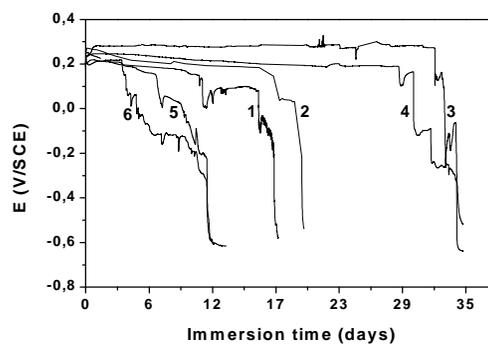


Figure 2 : Time evolution of the Open circuit potential for Ppy/oxalate-Ppy/large size counter ions duplex films electrosynthesized on iron electrodes. Test conditions are the same as in Fig. 1.

## REFERENCES

- [1] H. Nguyen Thi Le, B. Garcia, C. Deslouis and Q. Le Xuan\*, *Electrochimica Acta* (under press).
- [2] B. Garcia , H. Nguyen Thi Le, A. Lamzoudi, C. Deslouis, and Q. Le Xuan°, 199<sup>th</sup> ECS meeting, Washinton DC (march 2001).