

## Corrosion Protection by Poly(*ortho*-etoxyaniline)

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Polyaniline (PANI) and its derivatives exist in three oxidation states (leucoemeraldine – LE, emeraldine – EM and pernigraniline - PB), and in open air EM is the most stable one. The potential range of the EM coincides with the steel passivation potential range, and from that follows the emeraldine corrosion protection capacity *i.e.* polyaniline acts as a “chemical potentiostat” [1].

In this work the electrochemical investigation of poly(*ortho*-etoxyaniline) (POEA) has been carried out. The synthesis was carried out from 0.5 M *ortho*-etoxyaniline in 1.5 M H<sub>2</sub>SO<sub>4</sub> (POEASO<sub>4</sub>), and 3 M H<sub>3</sub>PO<sub>4</sub> (POEAPO<sub>4</sub>) by cycling from –400 mV to 1200 mV *vs.* Ag/AgCl. The substrate was stainless steel (13% Cr). The obtained POEA coating was studied by immersion of the coated sample in pure supporting electrolyte solution, and the open circuit potential ( $E_{oc}$ ) was monitored. As shown in Fig. 1 and Fig. 2, it is found that POEA, when in EM state, maintains the stainless steel potential in passive region, *i.e.* it stabilises the oxide layer formed on the substrate during the potential cycling.

It is also shown that in case of passivated steel, but not protected by POEA, within short time the potential decreases from the passivation potential region to the corrosion potential value.

The tests were carried out for different thickness of POEA layers and it was found that in sulphuric acid solution  $E_{oc}$  of the POEA coated stainless steel decreases towards corrosion potential, and the time of maintaining the passivation potential value depends on the thickness of POEA layer.

In case of POEA coating from phosphoric acid solution there was no decrease of  $E_{oc}$  from the passivation potential region towards corrosion potential value during the time of monitoring ( $\approx$  200 hours). It is known that the quality of the corrosion protection by conductive polymers, beside depending on the coating thickness, depends on the quality of the substrate [1-3], therefore the prolonged corrosion protection in phosphoric acid solution is attributed to the better protecting quality of the underlying oxide layer.

POEA coating on stainless steel has been studied by electrochemical impedance spectroscopy (EIS) to identify and characterise the oxidation states of POEA, POEA coating/metal interface, as well as the state of the metal surface. It was found that, by increasing the coating thickness, total impedance of the coating is lowered. This finding can be explained by the change of the LE/EM ratio in the polymer coating, and/or by the change in ratio of coated/free surface area. Capacitive behaviour, obtained for low frequency region is characteristic of the EM state. Capacitive component, as expected [4], decreases with the decrease in the coating thickness.

## References:

- [1] M.C. Bernard, S. Joiret, A. Hugot-Le Goff, P.V. Phong, *J. Electrochem. Soc.*, **148**, B12 (2001).
- [2] M. Kraljić, Z. Mandić, Lj. Duić, *Corros. Sci.*, **45**, 181 (2003).
- [3] D. W. DeBerry, *J. Electrochem. Soc.*, **132**, 1022 (1985).
- [4] H.N. Dinh, P. Vanysek, V.I. Birss, *J. Electrochem. Soc.*, **146**, 3324 (1999).

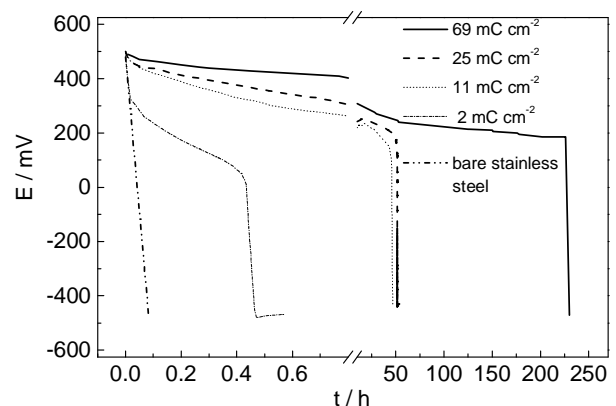


Fig. 1.  $E_{oc}$  vs. time for stainless steel coated by POEASO<sub>4</sub> and bare stainless steel in 1.5 M H<sub>2</sub>SO<sub>4</sub>.

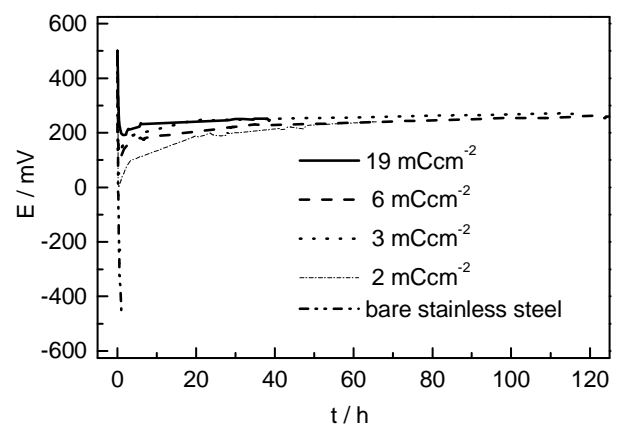


Fig. 2.  $E_{oc}$  vs. time for stainless steel coated by POEAPO<sub>4</sub> and bare stainless steel in 3 M H<sub>3</sub>PO<sub>4</sub>.

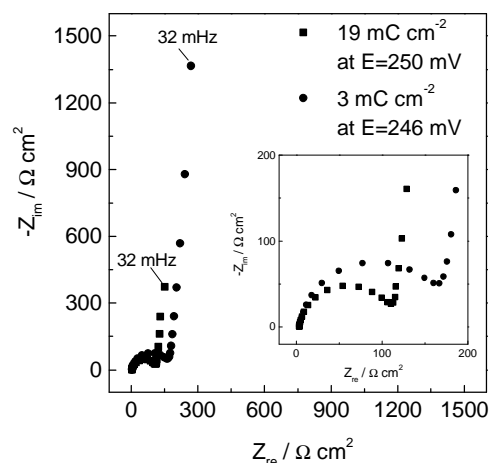


Fig. 3. Nyquist diagram for stainless steel coated by POEAPO<sub>4</sub> electrode in 3 M H<sub>3</sub>PO<sub>4</sub>.