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SHORT COMMUNICATION

Electropolymerization of pyrrole in aqueous solution on galvanized steel sheet

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1. Introduction

Following Lacaze *et al.* [1–3], zinc substrates may be covered by electropolymerized polypyrrole if first modified by potassium or sodium sulfide or ammonium sulfide. Deposits were obtained from sodium oxalate (0.1 M) solution containing 0.5 M pyrrole monomer. In this paper we consider galvanized steel sheet substrates.

2. Experimental details

The working electrode was made of various types of zinc alloy continuously hot-dip galvanized steel sheet (Cockerill Sambre). These are referred to, respectively, as spangled galvanized steel when the galvanization layer contained 0.1 wt% of aluminium, minimized spangle galvanized steel for a galvanization layer of 0.2 wt% Al and finally Galfan® when steel was covered with an Al–Zn eutectic of 4.5 wt% Al. Samples were 25 mm diameter discs degreased before use.

The reference electrode was a saturated calomel electrode (SCE) having a potential with respect to the normal hydrogen electrode (NHE) of +0.242 V. The counter electrode was a platinum grid (large area compared to the working electrode).

The aqueous solutions used for electropolymerization studies contained pyrrole (Aldrich 13, 170–9) first distilled under reduced pressure, and a supporting electrolyte, which was either oxalic acid (0.1 M) or sodium oxalate (0.1 M). Electrochemical experiments were performed with a Tacussel potentiostat (type PRT 20-2). A Dektak 3030 profilometer was used for thickness measurements. Compositions of the polymer films formed were determined using an Auger spectrometer (Physical Electronics, model 590).

Pretreatment of the various galvanized steels was performed before each electropolymerization with a solution of 0.1 M sodium sulfide (room temperature; 18 h). Without this pretreatment, no film could be formed. Pretreatment resulted in covering the galvanization layer with a sulfur containing passivating layer, as shown by EDS analysis.

3. Results and discussion

3.1. *Minimized spangle galvanized steel*

An oxalic acid (0.1 M) aqueous solution containing 0.1 M pyrrole monomer resulted in no film formation. The working electrode potential vs NHE was at first negative for about 150 s and later suddenly took very high positive values, of about +5.25 to +7.25 V vs NHE at a constant current density of 20 A m^{-2} [4]. This potential was much too high to allow polypyrrole layer formation on the surface. Moreover, black polypyrrole deposits were obtained inside the pits of the galvanized layer generated by this procedure. If a scratch was purposely drawn in the pretreated galvanized layer, that is, if the mild steel underlayer was in contact with the electropolymerization solution, a typical cauliflower like deposit was observed only at this scratch. This indirectly demonstrated the inhibiting character of the galvanizing layer for polypyrrole formation.

A 0.1 M sodium oxalate, 0.1 M pyrrole aqueous solution was then used. In this solution, an iridescent layer, yellow, green and purple in colour was formed after 10 min at a constant current density of 20 A m^{-2}. This was shown to be polypyrrole by Auger electron spectroscopy: carbon and nitrogen were detected, and, after a very short sputtering (Ar^+, 4 kV, 25 mA) a sulfur signal was also present, as shown in Fig. 1, due to the sodium sulfide pretreatment. However, no deposit was obtained at a fixed potential (+1.042 or +1.242 V vs NHE). The current density was between 5 and 10 A m^{-2} in this case. Auger electron spectroscopy again showed the presence of a sulfur containing layer due to the prior modification of the surface before electropolymerization.

In a 0.5 M pyrrole, 0.1 M sodium oxalate aqueous solution, a thick black film was formed either at a constant current density of 20 A m^{-2} or at a constant potential of +1.242 V vs NHE. This deposit had a cauliflower morphology as shown in Fig. 2. This morphology was characteristic of polypyrrole deposits. The working electrode potential vs NHE for a constant current density as a function of experiment duration is shown in Fig. 3. The potential values were, in contrast with the case of oxalic acid solution, compatible with the anodic formation of a polymer film from this monomer. Auger electron spectroscopy showed that films were formed after 30 min at +1.242 V vs NHE. They contained carbon and nitrogen. Argon ion sputtering for 5 min at 4 kV, 25 mA was not enough to reach the zinc containing substrate. No deposit was obtained at a potential value of +1.042 V vs NHE.

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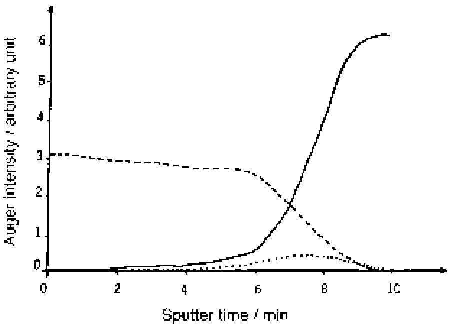

Fig. 1. Sputtering profile of a polypyrrole film formed on minimized spangle galvanized steel. Pretreatment of steel: 18 h in Na_2S. Electropolymerization conditions: 0.1 M $Na_2C_2O_4$, 0.1 M pyrrole aqueous solution; 600 s; 20 A m^{-2}, no agitation. Key: (·····) sulfur, (- - - -) carbon and (——) zinc.

3.2. *Spangled galvanized steel and Galfan®*

No deposit was obtained on these galvanized steel types for experiments of 30 min duration at +1.242 or +1.442 V vs NHE in a 0.5 M pyrrole, 0.1 M sodium oxalate aqueous solution. The same negative results were observed with solutions like those used for minimized spangle galvanized steel.

3.3. *Thickness measurements*

When deposits were obtained (sodium oxalate solution containing 0.5 M pyrrole monomer) they were characterized by a thickness measurement by profilometry. This result was compared to the calculated theoretical thickness based on electricity consumption to obtain the deposit (assuming a two-electron mechanism based on the monomer molecule implied in the process [5]), with a polypyrrole density of 1500 kg m^{-3} [5, 6] and a pyrrole molar mass of 6.5×10^{-2} kg mol^{-1}.

For a deposit obtained after 30 min at +1.242 V vs NHE, a theoretical value of 5.5 μm was calculated, showing a good fit with the measured value shown in Fig. 4 (5.5 μm). For a deposit obtained after 30 min at 20 A m^{-2}, the theoretical thickness was 8.1 μm while the experimental one was $10 \pm 2\,\mu$m as shown in Fig. 5. The agreement was also satisfactory.

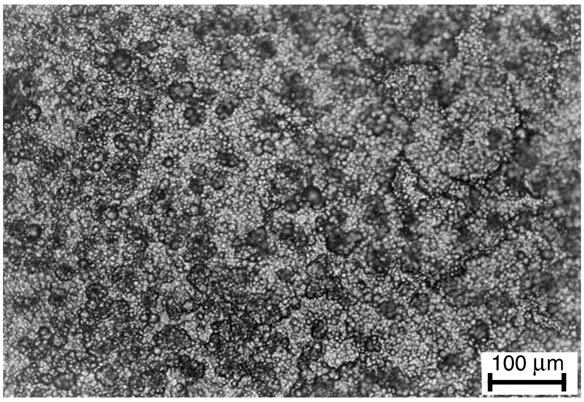

Fig. 2. Optical microscopy of an electropolymerized sample. Minimized spangle galvanized steel pretreated 18 h in sodium sulfide and electropolymerized 1800 s at +1.242 V vs NHE in 0.1 M sodium oxalate, 0.5 M pyrrole aqueous solution.

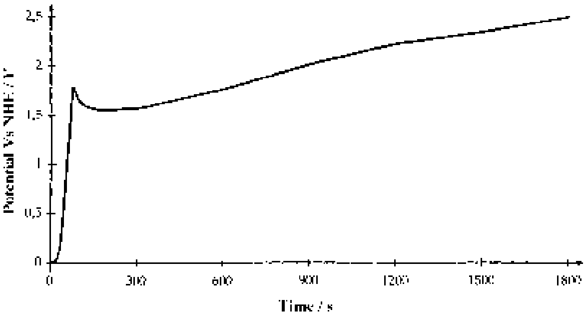

Fig. 3. Potential evolution for a working electrode vs NHE. Galvanostatic experiment (20 A m^{-2}). 0.1 M $Na_2C_2O_4$ and 0.5 M pyrrole aqueous solution. Substrate: minimized spangle galvanized steel pretreated 18 h in Na_2S.

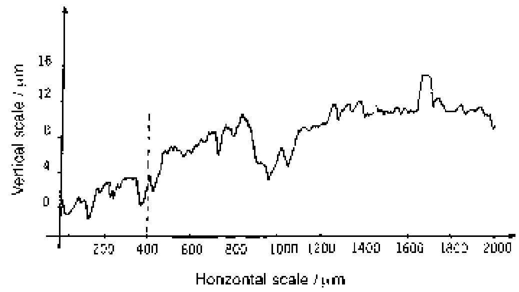

Fig. 4. Profilometry and step height measurement of a minimized spangle galvanized steel sample pretreated 18 h in Na_2S and electropolymerized for 1800 s at +1.242 V vs NHE in a 0.1 M $Na_2C_2O_4$, 0.5 M pyrrole aqueous solution.

4. Conclusion

On minimized spangle galvanized steel, no film was obtained in oxalic acid containing aqueous solution. In sodium oxalate containing aqueous solutions with a low monomer concentration (0.1 M), only galvanostatic conditions led to deposition. In contrast, a thick black deposit was formed both for galvano- and potentiostatic conditions if the sodium oxalate aqueous solution contained 0.5 M monomer.

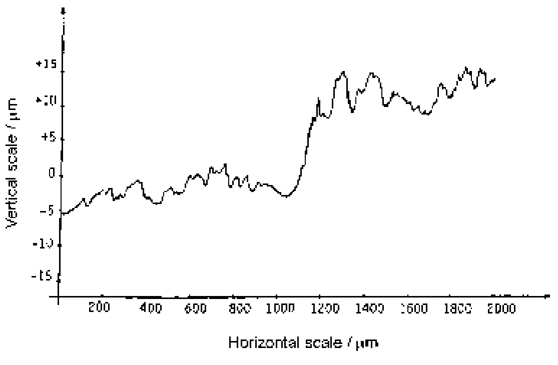

Fig. 5. Profilometry and step height measurement for a minimized spangle galvanized steel sample pretreated 18 h in Na_2S and electropolymerized for 1800 s at 20 A m^{-2} in a 0.1 M $Na_2C_2O_4$, 0.5 M pyrrole aqueous solution.

No deposit was obtained on spangled galvanized steel or on Galfan® even if the same pretreatment with sodium sulfide and the same conditions were applied as those leading to a film on minimized galvanized steel.

To obtain a polypyrrole film on galvanized steel, it is first necessary to form a passivating covering layer (probably here an insoluble zinc sulfide layer), and to make use of a not too acidic medium (to avoid pitting of the galvanized layer) containing a high enough monomer concentration. Moreover, with all these limitations, polypyrrole was only formed if the galvanized layer was of a minimized spangle type.

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