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Industrial polypyrrole electrodeposition on zinc-electroplated steel

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Abstract

Polypyrrole films were electrodeposited on zincated surfaces in a one-step process from aqueous solutions of sodium salicylate and pyrrole. This electrolyte passivates the substrate and makes it possible to obtain strongly adherent PPy films with controlled thickness by electrolysis at constant current. With a view to industrial application for rapid polymerization on common metals, an aqueous solution of 2 M sodium salicylate and 0.5 M pyrrole at pH 5 and room temperature provides optimum conditions. Laboratory studies and deposition with a pilot cell show that 2 μm of polymer can be deposited in 1 s with a current density of 70 A dm^{-2}.

1. Introduction

Because it is easy to control and to automate electrochemical processes industrially, there is a great deal of interest in direct electrodeposition of organic coatings from aqueous solution. In the anaphoretic or cataphoretic processes the electrocoagulation of water-dispersible paints results from a large pH shift in the diffusion layer due to electrochemical reactions such as oxidation or reduction of water [1]. Due to the insulating features of the films obtained, these methods are widely used in industry, but require thermal curing of the paints after deposition. To reduce the number of steps needed and to achieve close control of the finished coating, efforts have been made in recent years to realise polymerization *in situ*. To this end the electrosynthesis of conducting polymers such as polyaniline (PAni), polythiophene (PT) or polypyrrole (PPy) has been considered. Among these coatings, PPy presents high industrial potential owing to the low monomer toxicity, its high stability in the oxidized state and its ease of synthesis in aqueous solution [2–5].

However, as these films are produced by an oxidative process, the nature of the electrode is a critical consideration. Indeed, in the case of common metals such as Fe, Al and Zn it is important that the electrode is not oxidised concurrently with the monomer. Preliminary studies demonstrated that careful choice of the solvent, the electrolyte [6–8] and the electrode treatment [9–11] is necessary in order to passivate the metal without preventing electropolymerization.

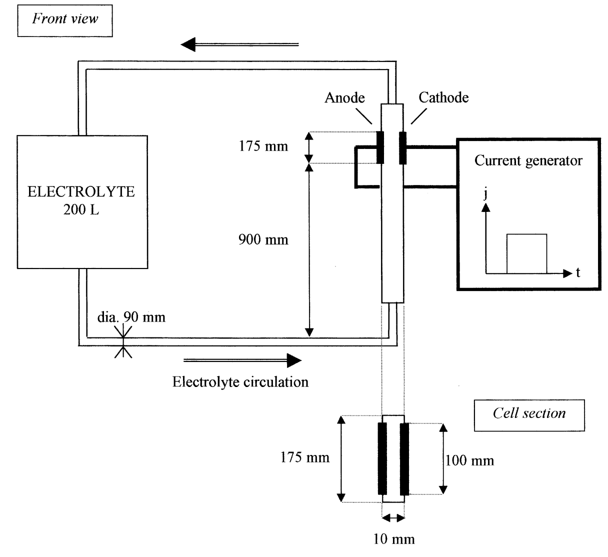
For zinc or zincated surfaces, which are widely used industrially, the use of an aqueous solution of 1 M sodium salicylate (NaSac) and 0.5 M pyrrole (Py) at pH 5 allows the formation of strongly adherent PPy coatings with high current densities and without metal dissolution [12]. In view of these results, industrial production of PPy-coated zincated steel is envisaged by USINOR to replace the classical conversion treatments (phosphatation and chromatation). To this end, it is necessary to deposit the coating under the specific hydrodynamic conditions associated with the rapid passage of steel sheet through radial cells (about 100 m min^{-1}). Moreover, high polymerization rates are required, of the order of 2 μm of polymer in 3 s.

In this paper we demonstrate that it is possible to optimize the polymerization conditions to satisfy these criteria. Laboratory simulations of the production conditions and polymerization tests with a USINOR pilot cell are reported.

2. Experimental details

2.1. *Laboratory studies*

Sodium salicylate and salicylic acid were purchased from Acros and used without further purification. Pyrrole (Acros) was distilled twice under argon. Water was purified by passing through a Millipore purification system.



Scheme 1. Description of the CEC set-up.

All voltammetric and galvanostatic experiments were performed using a one-compartment three-electrode cell driven by a Princeton Applied Research (PAR) model 363 potentiostat/galvanostat and model 175 universal programmer connected to a Sefram TGM 164 XY recorder. The working electrode was a zinc (dia. 0.5 cm and polished with 1200 grit paper), a 7.5 or 10 μm zinc-electroplated steel (dia. 1 cm) or a platinum disc (dia. 0.3 cm and polished with 1 μm diamond paste). The counter-electrode was a stainless-steel plate and the reference electrode a Tacussel KCl saturated calomel (SCE). The rotating disc electrode (RDE) was a EDI 101 radiometer monitored with a CTV 101 radiometer speed control unit.

Bath conductivities were determined with a 702 KNICK conductometer.

2.2. *Industrial studies*

Sodium salicylate (66.3 kg) and pyrrole (6.9 L) were purchased from Jansen and used without further purification. The volume of electrolyte used was 200 L.

Galvanostatic experiments were carried out with a USINOR pilot cell: a circulating electrolyte cell (CEC, Scheme 1). In contrast with the industrial line where the steel sheet passes through the cell with a speed of about 80 m min^{-1}, the 10 μm zinc-electroplated steel working and counter electrodes (175 mm × 100 mm) were motionless and the electrolyte circulated. The gap separating the electrodes was fixed at 10 mm.

3. Results and discussion

Initial work performed with USINOR demonstrated that the hydrodynamic conditions of a production line could be adequately simulated in the laboratory with a RDE. Figure 1 presents the correlation between the electrode rotation speed (ω) and sheet speed (v_s)*. It should be noted, however, that the theoretical ω value needed to simulate the industrial v_s value (100 m min^{-1}) is very high (about 5300 rpm) and consequently difficult to achieve in the laboratory.

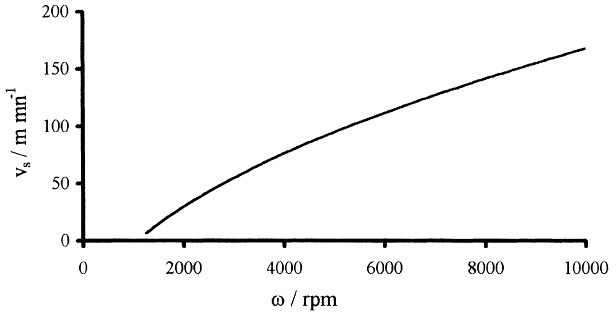


Fig. 1. Correlation between the electrode rotation speed (rpm) and the sheet speed (m min^{-1}).

3.1. *Effect of the electrode rotation speed (ω)*

3.1.1. *Voltammetric behaviour*

We first determined the influence of the rotation speed on the voltammetric curve shape obtained on a zinc electrode in an aqueous solution of 1 M NaSac and 0.5 M Py at pH 5 (scan rate 10 mV s^{-1}). Figure 2(a) presents the characteristic voltammogram for a motionless electrode [12] which shows three main oxidation peaks at −0.9, −0.65 and 0.5 V (noted P1, P2 and P3, respectively), one oxidation wave beginning at 0.6 V (noted W1) and one reduction peak at −0.9 V (noted P4). P1 and P2 are representative of the passivation process and correspond to zinc oxidation inducing the formation on the electrode surface of a passivating layer consisting of a 1:1 zinc-salicylate complex [13].

P_3 can be attributed to a synergetic effect of pyrrole, sodium salicylate and the zinc electrode, because this peak is absent on a platinum electrode or when there is no monomer in the solution. Our recent investigations have demonstrated that this peak comes from the simultaneous oxidation of zinc, salicylate ion and Py, inducing a transition from a zinc electrode to a PPy-coated zinc electrode. The formation of a thin PPy film leads to a marked modification of the electrochemical processes at the electrode, W_1 and P_4 correspond to the oxidation of solubilized pyrrole and to polymer reduction, respectively.

When the electrode rotates (from 0 to 4000 rpm), the rotation speed has little effect on the voltammogram which remains similar to that obtained for a static configuration (Figure 2(b)). The P1 and P2 peak intensity decrease demonstrates that electrode rotation does not facilitate the solubilisation of the passivating species but increases the efficiency of the passivation step.

In all cases, pyrrole oxidation leads to the formation of strongly adherent and homogeneous polypyrrole

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[*] Private communication from LEDEPP (USINOR–SACILOR).

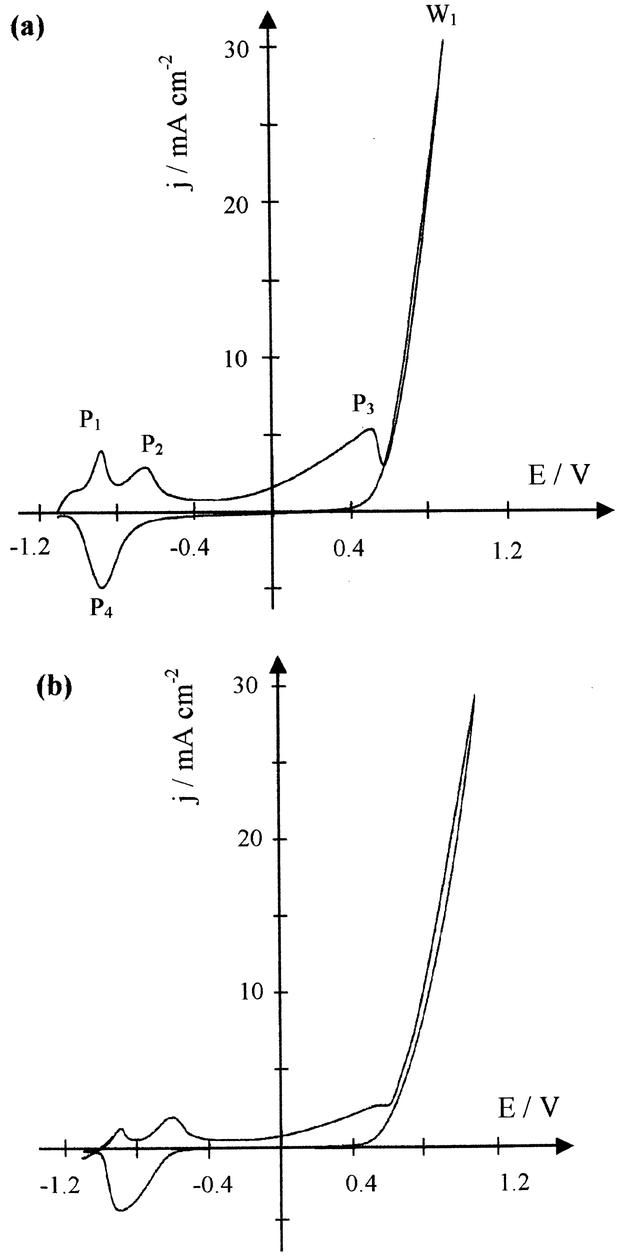

Fig. 2. Cyclic voltammograms on a zinc electrode (dia. 0.5 cm, polished with 1200 grit paper) in an aqueous solution of 1 M NaSac and 0.5 M Py at pH 5. (a) $\omega = 0$ rpm; (b) $\omega = 4000$ rpm. (Scan rate: 10 mV s^{-1}).

coatings. SEM micrography (Figure 3) shows that rotation gives a more compact polymer than that obtained with the static configuration.

3.1.2. *Galvanostatic behaviour*

For a current density of 5 mA cm^{-2}, and independently of the electrode rotation speed (from 0 to 4000 rpm), the potential stabilizes at around 0.65 V. Homogeneous and strongly adherent polymers are deposited on the zinc electrode.

The variation of the thickness (e_{PPy}, determined from micrographic cuts) with the synthesis time (t_s) is in good agreement with the theoretical values given by Faraday's

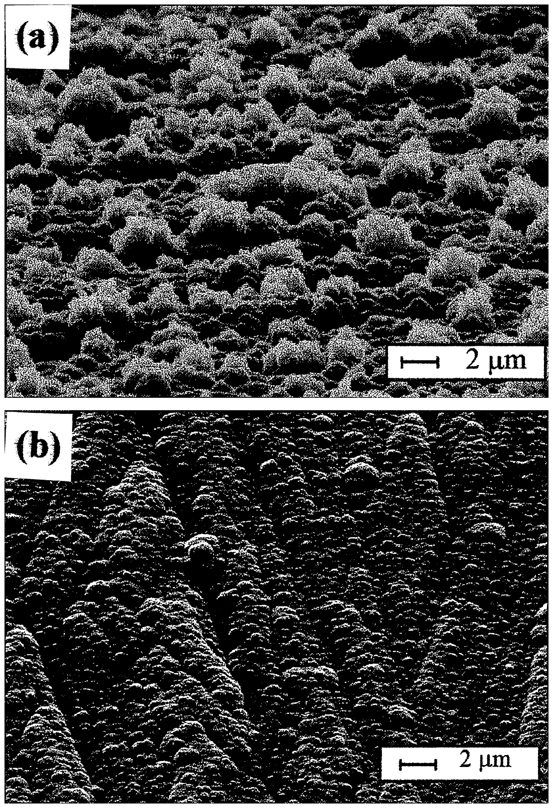

Fig. 3. SEM micrographs of polypyrrole doped by Sac^-: (a) $\omega = 0$ rpm; (b) $\omega = 4000$ rpm.

law (Equation 1). The film growth rate is 1 μm $\min^{-1}$ corresponding to a charge $q = 0.3$ C cm^{-2} for the synthesis of 1 μm of PPy [12, 13]. The thickness is given by

$$e_{\mathrm{PPy}} = \left(\frac{M_{\mathrm{Py}} + yM_{\mathrm{Sac}}}{F\rho(2+y)}\right) jt_s \tag{1}$$

where F is the faradaic constant, ρ the polymer density (1.5 g cm^{-3} [14]), y the doping level (0.22) [12], M_{Py} the molecular weight of pyrrole unit (65 g mol^{-1}), M_{Sac}, the molecular weight of salicylate (137 g mol^{-1}) and j the current density.

Because the compatibility of the galvanostatic mode with the hydrodynamic conditions of production and the ease of control under laboratory conditions of the film thickness via the current density and the time of synthesis, the galvanostatic mode appears to be the most promising way of using the present electrodeposition process industrially.

For the high polymerization speed required ($e_{\mathrm{PPy}} = 2$ μm in 3 s), given the above q value, it is possible to calculate the theoretical current density, $j = 20$ A dm^{-2}. Such a condition appears prohibitive, since a reaction-limited current density of a few mA cm^{-2} [15] has been repo rted in wet acetonitrile, but we will show that high current densities are readily obtained in aqueous media.

3.2. *Effect of sodium salicylate and pyrrole concentrations*

In all cases, the pH was held at 5 because (i) pyrrole polymerizes readily at this value [16, 17], (ii) the passivation efficiency decreases above this value (with an increase of the P_1 and P_2 peak intensities) and (iii) sodium salicylate is soluble and dissociated ($pK_a = 2.97$) [18, 19].

Electrolysis was run at room temperature (T_r) to avoid (i) loss of passivation resulting from an increase in the solubility of the zinc–salicylate complex with an increase in temperature; (ii) monomer evaporation and (iii) decrease in salicylate solubility below T_r. Moreover, this condition avoids spending energy on the thermal regulation of the industrial bath.

3.2.1. *Variation of the polymerization rate (R_p)*

To determine the effect of the monomer and electrolyte concentrations on the rate of PPy synthesis, we examined how the voltammogram on Pt or Zn electrodes varies with the pyrrole concentration [19, 20] for two electrolyte concentrations (0.1 and 2 M) and different salts (sodium salicylate and lithium perchlorate).

If the water discharge is neglected and a quantitative faradaic yield assumed, a linear relation between the electrical charge consumed per electrode unit area (Q) and the weight of polymer produced per unit area (M) can be written as

$$Q = k'M \tag{2}$$

with k' a constant (electrical charge spent to generate a unit of polymer mass).

For a fixed potential on the voltammogram, the current density for pyrrole oxidation can be expressed as follows:

$$j = \frac{dQ}{dt} = k'\frac{dM}{dt} = k'R_p \tag{3}$$

Table 1. Reaction orders of pyrrole as a function of the electrode nature and rotation speed (rpm), electrolyte structure and concentration (M)

Electrolyte	Concentration/M	Electrode		Reaction order (α)
		Nature	ω/rpm	
Sac^-	0.1	Pt	0	0.6
	2	Pt	0	4.2
	2	Zn	0	2.3
	2	Zn	2500	3.1
ClO_4^-	0.1	Pt	0	0.5
	2	Pt	0	0.8

where R_p, the electropolymerization rate, which is described empirically as a function of the monomer and electrolyte concentrations [19, 21], that is,

$$R_p = k[Py]^{\alpha}[E]^{\beta} \tag{4}$$

where [Py] and [E] are the pyrrole and electrolyte concentrations, k is an apparent kinetic constant, and α and β the monomer and electrolyte reaction orders.

Figure 4 shows how the voltammogram varies with the pyrrole concentration (from 0.1 to 0.5 M) for a platinum electrode in an aqueous solution of 0.1 M NaSac (scan rate 10 mV s^{-1}). Between [Py] = 0.5 and 0.2 M, reducing the concentration leads to a regular decrease in the pyrrole oxidation current density. For [Py] = 0.1 M, the current density falls abruptly. This behaviour appears to be specific to the salicylate anion, since it does not occur with lithium perchlorate.

According to Equation 4, the monomer reaction order corresponds to the slope of the linear relationship observed between ln (j) and ln [Py] at different potentials (for a monomer concentration greater than 0.2 M). The corresponding result is presented in Table 1 and is close to that determined under the same experimental conditions with lithium perchlorate.

To evaluate the effect of the electrolyte on the polymerization rate, the same approach was used with a high salicylate or perchlorate concentration (2 M).

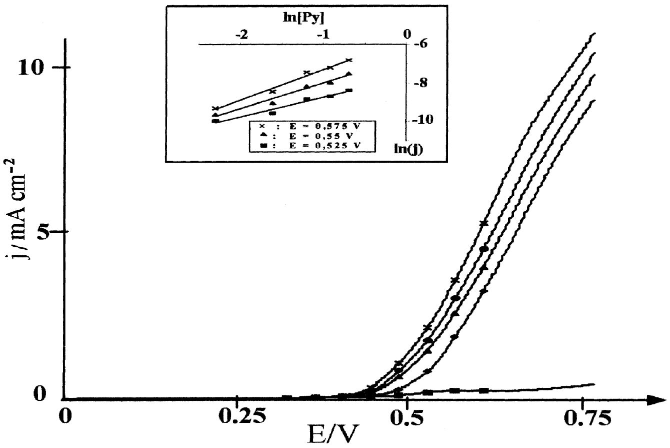

Fig. 4. Anodic voltammograms obtained by a linear sweep of potential on platinum (dia. 0.2 cm) in an aqueous solution of 0.1 M NaSac at pH 5 for different pyrrole concentrations: (■) 0.1, (◆) 0.2, (▲) 0.3, (●) 0.4 and (∗) 0.5 M. (Scan rate: 10 mV s^{-1}).

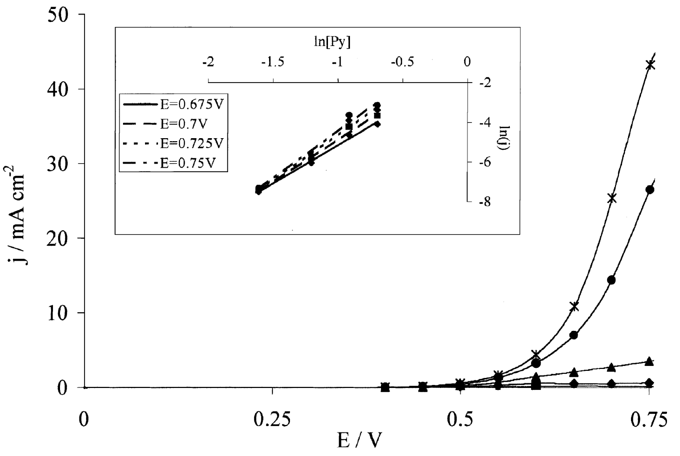

Fig. 5. Anodic voltammograms obtained by a linear sweep of potential on platinum (dia. 0.2 cm) in an aqueous solution of 2 M NaSac at pH 5 for different pyrrole concentrations: (■) 0.1, (◆) 0.2, (▲) 0.3, (●) 0.4 and (*) 0.5 M. (Scan rate: 10 mV s^{-1}).

For a fixed potential and monomer concentration, an increase in the pyrrole oxidation current with the electrolyte concentration is observed, corresponding to an increase in the corresponding R_p value. For [NaSac] = 2 M (Figure 5), the monomer oxidation wave at Pt electrode appears to be strongly dependent on [Py]. Indeed, the α parameter determined in this case is seven times greater than that calculated for 0.1 M electrolyte (Table 1). This effect on the R_p value can be attributed to the salicylate anion, since this behaviour is not observed for 2 M $LiClO_4$, and appears to depend slightly on the electrode nature and rotation (Table 1). These results indicate that [NaSac] and [Py] must be as high as possible to obtain fast PPy film electrodeposition and that the higher the electrolyte concentration, the more sensitive R_p is to [Py].

3.2.2. *Optimization of the electrodeposition bath concentrations*

Since a high current density is needed to deposit polymer as fast as possible, the bath conductivity (σ) must be high to avoid power loss through the Joule effect. The variations of σ with the sodium salicylate and pyrrole concentrations were studied. For [Py] = 0.5 M, the conductivity increases by 35% between [NaSac] = 1 and 2 M (from 37 to 50 S cm^{-1}) and remains approximately constant up to 4 M (maximal salt solubility). Moreover, the monomer concentration does not significantly modify the conductivity.

For [NaSac] > 1 M and different bath compositions, pyrrole was polymerized in the galvanostatic mode on zinc-electroplated steel rotating electrodes (from 1250 to 4000 rpm) for t_s = 3 s and variable current densities.

We observed that high monomer concentrations facilitate the use of high a current density. For example, for an aqueous solution of 1 M NaSac, the maximum current density usable with [Py] = 0.1 M is 1 A dm^{-2} (a greater j value overloads the potentiostat, $E > 10$ V, and no polymer deposition) as against 25 A dm^{-2} for [Py] = 0.5 M.

However, above [Py] = 0.5 M, in spite of the fact that the potential quickly stabilizes and polypyrrole is formed homogeneously on the electrode, the coating adherence appears to depend on the current density and the bath composition. For each case, there is a maximum current density (j_{max}) beyond which the polymer loses its adherence (Table 2). The adherence of PPy films was tested by the AFNOR NFT 30038 Sellotape test after criss-crossing the covered metallic surface.

The electrolyte concentration has a marked effect on the j_{max} value. For [Py] = 0.5 M, j_{max} increases by 220% on going from [NaSac] = 1 to 2 M and thereafter remains constant.

The pyrrole concentration also affects this maximum current density. From [Py] = 0.5 M to [Py] = 1 M, j_{max} falls by 75% for [NaSac] = 2 M. This fall is compensated by increasing [NaSac]. For higher monomer concentration, as illustrated with [Py] = 2 M (maximum of solubility), j_{max} remains very low even for the highest salicylate concentration (Table 2).

These variations underline that a balance has to be struck between the pyrrole and sodium salicylate concentrations to get a coating which adheres to the electrode.

3.3. *Choice of the industrial electrolytic bath composition*

The above studies allow the determination of two optimal polymerization conditions:

Table 2. j_{max} (A dm^{-2}) variation with sodium salicylate and pyrrole concentrations. j_{max} corresponds to a maximum current density beyond which the polymer loses its adherence

		j_{max}/A dm^{-2} [NaSac]/M			
		1	*2*	*3*	*4*
[Py]/M	0.5	25	80	80	80
[Py]/M	1		20	50	65
[Py]/M	2				25

(a) [Py] = 0.5 M and [NaSac] = 2 M at pH 5 and T_r

(b) [Py] = 1 M and [NaSac] = 4 M at pH 5 and T_r.

These conditions lead to a maximal bath conductivity (50 S cm^{-1}), high j_{max} value (80 and 65 A dm^{-2}, respectively) and good passivation efficiency.

According to the electrodeposition rate study, condition (b) accelerates polymerization and should be the better. However, in industry the price of the electrolyte solution is a crucial criterion for choosing between the two polymerization conditions. In this case, bath (a) is cheaper (15 euro L^{-1} against 30 euro L^{-1} for bath (b)) and was tested under production conditions.

3.4. *PPy coating synthesis on rotating disc electrode under industrial conditions*

The angular speed of the electrode was fixed at 4000 rpm. Pyrrole was polymerised (t_s = 3 s) on the zinc-electroplated steel with variable current density (from 10 to 70 A dm^{-2}). The thickness (e_{PPy}) was determined from micrographic cuts and SEM. The theoretical (calculated from Equation E1) and experimental values are reported in Figure 6. There is good agreement between experiment and theory, indicating that the electrical yield is 100% in spite of the high current density used and, consequently, that it is possible to control the polymer thickness exactly by means of the current density as easily as under laboratory conditions. This means that the current could be used to control the thickness of the coating or to deposit the same thickness of PPy at a higher sheet speed (e_{PPy} = 2 μm and $t_s \sim 1$ s for j = 70 A dm^{-2}).

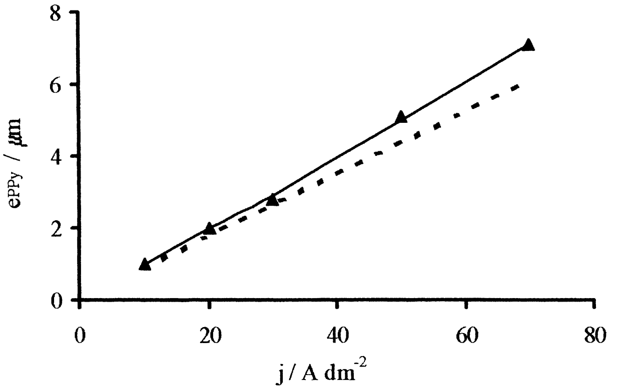

Fig. 6. PPy thickness dependence on current density for t_s = 3 s. (- - - -) Theoretical and (—) experimental.

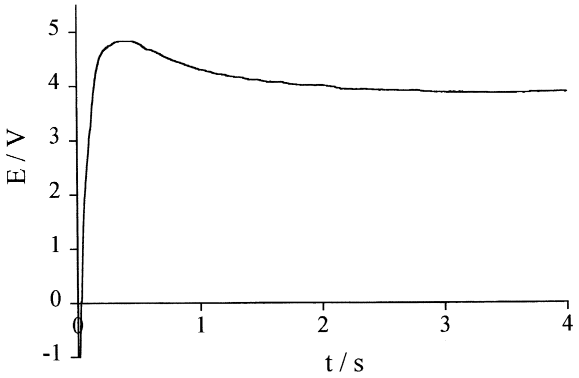

Fig. 7. Galvanostatic behaviour of a 0.8 cm^2 zinc electroplated steel electrode in an aqueous solution of 2 M NaSac at pH 5 for j = 20 A dm^{-2} and ω = 4000 rpm.

The j = 20 A dm^{-2} condition corresponds to the industrial requirements: e_{PPy} = 2 μm and t_s = 3 s. In this case, the polymerization potential is about 4 V (Figure 7), the polymer formed is homogeneous (Figure 8) and adheres strongly to the substrate.

Another important aspect of this process is its independence of the surface roughness and the composition of the substrate. Several zinc electrodes (provided by USINOR) with various surface states were tested. In all cases, film was deposited under the same conditions as with polished samples. Furthermore, the process was successful with other metallic substrates such as iron, mild steel, zinc/cobalt, zinc/nickel, zinc/aluminium, aluminium, copper and tin, and the same electrochemical behaviour as with zinc substrate was observed.

3.5. *PPy coating synthesis with the CEC USINOR pilot cell*

Electrodepositions were carried out with a pilot cell: the 'circulating electrolyte cell' (described in Section 2.2). As

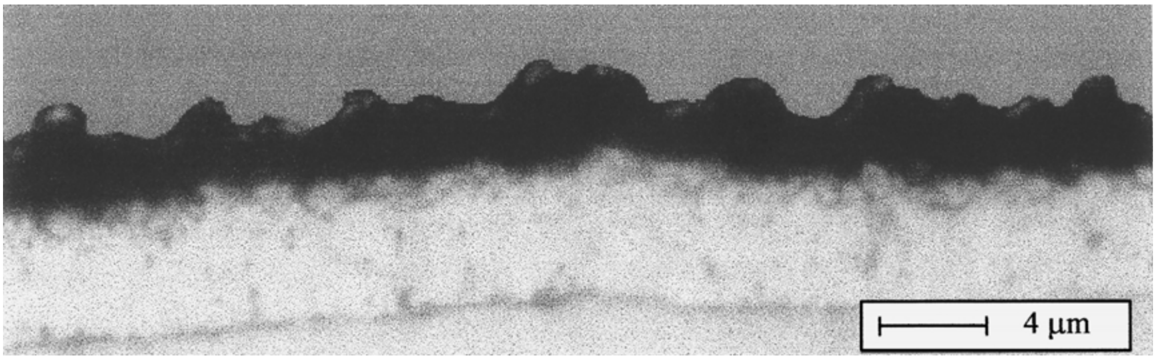

Fig. 8. Micrographic cut of PPy doped by Sac^- and synthesized with j = 20 A dm^{-2}, t_s = 3 s and ω = 4000 rpm.

with the RDE, to facilitate the transposition of the experimental results from the CEC to the production line, a linear correlation was established between the flow rate (v_e) and the sheet speed (v_s). Then, to simulate a large range of hydrodynamic conditions, films were deposited with v_e ranging from 150 m min^{-1} (corresponding to $v_s = 40$ m min^{-1}) to 450 m min^{-1} (corresponding to $v_s = 150$ m min^{-1}).

Polypyrrole coatings were synthesized with the above optimised electrolyte bath: 2 M NaSac, 0.5 M Py, pH 5 and $T = T_r$. The time and current density used were as previously: $j = 20$ A dm^{-2} and $t_s = 3$ s. To avoid variation of the polymerization conditions due to evaporation of the monomer, the pyrrole concentration was regularly determined, by comparing the voltammogram obtained in the industrial bath on a zinc electrode with those determined in preliminary experiments at different pyrrole concentrations, and corrected.

Experiment demonstrated that the same electrolyte solution can be used for several days without degradation as long as the pyrrole concentration is maintained at 0.5 M by addition of monomer, a particularly important result for continuous deposition.

In all cases, satisfactory polypyrrole coatings were formed on the electrode. SEM micrographs revealed the same morphology as those obtained with the RDE. The thickness, determined by micrographic cuts, was close to the theoretical value (2 μm). The fact that effect of flow rate on the electrodeposition efficiency is small confirms that the process could be adapted to different production speeds.

4. Conclusion

The use of an aqueous sodium salicylate solution as electrolyte allows the formation of adherent and homogeneous PPy films on zinc, zinc-electroplated steel and a large variety of common metals [22] in a one-step process. Sodium salicylate complexes the metal ion arising from electrode oxidation to form a thin protective layer which slows further dissolution of the metal considerably, but does not prevent oxidation of the monomer.

Optimization of the bath composition to satisfy industrial criteria (polymerization rate and bath price) led to the choice of an aqueous solution of 2 M NaSac and 0.5 M Py at pH 5 and room temperature. Laboratory simulation (with a RDE) revealed that the reaction current efficiency is 100% for the galvanostatic synthesis procedure (independently of the current value) and that it is possible to achieve ultrafast pyrrole electropolymerization (2 μm in 3 s at 20 A dm^{-2}) under hydrodynamic conditions corresponding to those of a production line. This was confirmed by the results obtained with the USINOR pilot cell (CEC) [22].

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