



Cyclic potential sweep electrolysis for formation of poly(2-vinylpyridine) coatings

X. LING**, M.D. PRITZKER*, C.M. BURNS and J.J. BYERLEY

Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

*(*author for correspondence)*

***present address: Clariant Corporation, 70 Meister Avenue, Somerville, New Jersey 08876, USA)*

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Abstract

A cyclic potential sweep (CPS) technique has been used to form coatings of poly(2-vinylpyridine) on mild steel substrates by electropolymerization of the monomer. This method can produce thick and uniform coatings of much higher quality than can be formed by other electrochemical methods such as galvanostatic electrolysis, constant cell-potential electrolysis and chronoamperometry. The range and rate of the potential sweep during the CPS are important for successful coating formation. Potential sweeps between -1.0 and -2.2 V vs SCE at rates from 10 to 50 mV s^{-1} have been found to be most suitable for the formation of poly(2-vinylpyridine) coatings. The essential reason for the successful application of the CPS technique to the electropolymerization process is the compatibility of the nature of the CPS process and the mechanism of 2-vinylpyridine electropolymerization.

1. Introduction

Formation of polymer coatings by electropolymerization has attracted considerable attention due to its important applications in many areas [1–10]. To form a high quality coating by electropolymerization, it is important to use the proper electrochemical technique. The most commonly used electrochemical methods include galvanostatic electrolysis, chronoamperometric electrolysis, constant cell-potential electrolysis and cyclic potential sweep (CPS) electrolysis. The principles of these methods are well known [5, 11, 12]. A proper electrochemical technique should be one that is intrinsically compatible with the reaction mechanism of electropolymerization.

The primary reason for using a galvanostatic technique for electropolymerization is that it theoretically allows control of the supply of radicals generated by electrochemical reactions [13–16]. However, when the polymer film on the electrode surface is poorly conducting, a voltage drop occurs across the coating, leading to a variation in the effective potential for radical generation. This makes the process more difficult to control, particularly when radical generation can occur throughout the film and the potential on the working electrode is

not being controlled, as is the case during galvanostatic electrolysis [5].

Simplicity of the instrumentation and operation is the most distinct advantage of the constant cell-potential technique. This technique has been used to form polyoxyphenylene coatings [17–20], poly(acrylonitrile-co-acrylic acid) coatings [21], poly(*o*-allylphenol) coatings [22], and a variety of aniline-, phenol- and vinyl-type polymer coatings [7]. The shortcoming of this technique is that it allows no control over the working electrode potential during the electrolysis and hence current and radical generation cannot be directly controlled. When a polymer coating forms on the electrode surface, the current and the electrode potentials of both the working and the counter electrodes will vary to maintain the cell-potential at the preset value. This may change the electrochemical processes on the electrodes and may cause some undesired side-reactions to occur.

Chronoamperometric electrolysis is widely used in electrochemical processes. The advantage of this technique is that the working electrode potential can be closely controlled for the desired electrochemical processes. It has often been used for coating formation via electropolymerization [8, 9, 23, 24]. It may be difficult, however,

to choose one constant electrode potential that is optimum for an entire process when coatings are being formed. For example, de Bruyne et al. [9] reported that the current during electropolymerization of 2-vinylpyridine starts at a very high value and drops quickly after the onset of the electrolysis. This suggests that a large supply of radicals is generated at the beginning, with much fewer being produced for the remainder of the process. When a large supply of radicals is generated in a short period, excessive termination may occur leading to a low initiation efficiency. In an effort to overcome this shortcoming, we developed a modified chronoamperometric technique and applied it to the formation of poly(2-vinylpyridine) coatings on mild steel [10]. The technique involved holding the mild steel electrode potential at a constant cathodic value for a period of time and then slowly ramping the potential linearly in the positive direction to complete the process. This led to a reduction in the extent of hydrogen evolution during electropolymerization and an improvement in the morphology of the coating.

Cyclic potential sweep (CPS) electrolysis involves the repeated application of triangular potential waveforms to the working electrode. Numerous applications of CPS to polymer coating formation have been reported. Abruna et al. [1] and Denisevich et al. [25] formed polymer coatings from vinylpyridines and iron and ruthenium vinylpyridine complexes. McCarley et al. [26] used this method to form osmium vinylpyridine coatings, while Huang et al. [27] formed poly(1-naphthylamine) films. Ohno et al. [28] found that halogenated xylene coatings prepared by CPS were more corrosion resistant than those produced by galvanostatic electrolysis. Another advantage of this technique is that the system response of current vs. time (or electrode potential) is composed of a series of voltammograms that can provide diagnostic information on the reaction mechanism.

The modified chronoamperometric method used in our previous study [10] is similar to CPS electrolysis to the extent that the electrode potential is varied during electropolymerization in an effort to improve the process. In view of our success with the use of this method for poly(2-vinylpyridine) coating formation, we have conducted a comprehensive study of the use of CPS electrolysis for the formation of poly(2-vinylpyridine) coatings on mild steel. In this paper, we focus particularly on the effects of CPS electrolysis on coating morphology and on determining the optimum potential sweep range and rate for the electrolysis. These results are interpreted in terms of the process mechanism that was proposed in our earlier studies of this system [10, 29].

2. Experimental details

The detailed experimental set-up, the procedures of chemical purification, electrode preparation, and coating post-treatment and characterization have been reported elsewhere [10, 29]. After dissolving 2-vinylpyridine in a 20 vol. % methanol aqueous solution to make a 0.25 M solution, 0.05 M NH_4ClO_4 was added along with enough concentrated HClO_4 to adjust the solution pH to 4.8. The electrode potentials reported were all referred to the standard calomel electrode (SCE) scale. All samples have an active surface area of 5.5 cm^2 . The electrolyte was continuously agitated with a magnetic stir bar throughout the electrolysis and was maintained at 20 °C. Coating morphology and thickness were examined by confocal scanning laser microscopy (CSLM) [30]. The effects of the range of the working electrode potential during a CPS electrolysis were studied by adjusting one potential limit while keeping the other constant. The potential sweep rate was maintained at 30 mV s^{-1} during this phase of the experiments. The effects of the potential sweep rate were studied over a range from 5 to 100 mV s^{-1} , while fixing the potential scans between -1.0 and -2.2 V.

3. Experimental results and discussion

3.1. General results

The experiments on polymer coating formation using the galvanostatic, constant cell-potential and chronoamperometric methods met with limited success. The primary difficulty was that intense hydrogen evolution occurred at the electrode surface due to the improper value of electrode potentials. The polymer coatings formed were thin and non-uniform. A modified chronoamperometric technique did improve the coating quality to a certain extent. As described previously, the coatings were thicker and the craters formed on the coating surface due to evolution of hydrogen (H_2) gas bubbles during electropolymerization were partially filled [10]. A summary of the results obtained using these different electrochemical methods (including the CPS technique) is given in Table 1.

A typical CPS electrolysis is carried out in the potential range of -0.7 and -2.5 V at a sweep rate of 30 mV s^{-1} . Thus, a cycle is completed every 2 min. An I/t response for such a process is shown in Figure 1. The I/t diagram can provide important electrochemical information on the working electrode during the process through the changes in the current response. The circled regions labeled (a), (b) and (c) in Figure 1 are shown in

Table 1. Summary of different electrochemical techniques for coating formation

Electrochemical technique	Result
Galvanostatic	Difficulty in choosing a proper constant current. Intense hydrogen evolution and no coating generation
Constant cell-potential	Floating electrode potentials and poor experimental reproducibility
Chronoamperometry	Intense hydrogen evolution (at high potential) or thin coating (at low potential)
Modified chronoamperometry	The hydrogen pits in the coating are refilled to a certain degree, and uniform coating formed
Cyclic potential sweep	Thick and uniform coating formed

enlarged form in Figures 2(a), (b) and (c). It is clear from Figures 1 and 2(a) that the current drops rapidly during the first few cycles. This is likely due to the formation of a resistive polymer coating on the electrode surface. The current then reaches a condition in a few minutes where the system gives a similar current response from one cycle period to the next (Fig. 2(b)), but slowly changes over time (Fig. 2(c)). The current response during the first cycle (Fig. 2(a)) shows a simple monotonic rise during the cathodic-going portion (from

$t = 0$ to $t \sim 1$ min) followed by a decline during the anodic-going portion (from $t \sim 1$ min to $t \sim 2$ min). Thereafter, a more complex response becomes visible. Two distinct portions appear during the cathodic-going portion of the second cycle: a well-defined plateau from $t \sim 2.1$ min to $t \sim 2.7$ min followed by a steeper current rise that reaches a maximum when the scan direction is reversed in the anodic direction (i.e., $t \sim 3.1$ min). The plateau develops into a peak (e.g., at $t \sim 58.5$, 60.5 and 62.5 min in Fig. 2(b)) before becoming a shoulder in the later stages of electrolysis (Fig. 2(c)). Regardless of the appearance of this current rise, its half-wave potential remains at approximately -1.0 V during each cycle, which has been shown to be associated with the reduction of 2-vinylpyridine [10, 29].

The second current rise that reaches a maximum when the scan is reversed in the anodic direction occurs at potentials where H_2 evolution was observed to occur in our earlier studies [10, 29]. It is also evident in Figure 2(b) and (c) that some additional structure (i.e., shoulder) develops in this part of the response although one cannot be certain of its origin. Nevertheless, this part of the response tends to be pushed toward later times during each cycle as the electrolysis proceeds. This observation is consistent with the fact that the formation of the poly(2-vinylpyridine) coating suppresses hydrogen evolution, leading to a higher overpotential. Importantly, much less hydrogen evolves from the mild

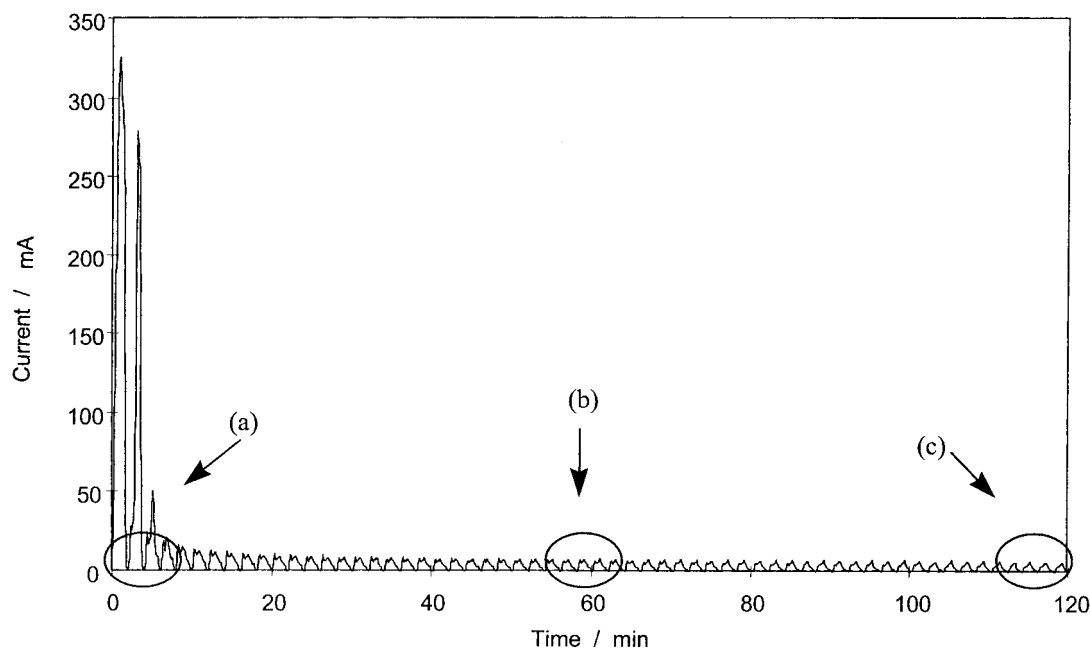


Fig. 1. Typical I/t diagram during a CPS electrolysis. Cathodic potential sweep range is between -0.7 and -2.5 V and sweep rate is 30 mV s^{-1} . The electrolyte contains 0.25 M 2-vinylpyridine and 0.05 M NH_4ClO_4 in 20% methanol aqueous solution at pH 4.8 (adjusted with HClO_4). Circled segments (a), (b) and (c) indicate the three segments that are enlarged and shown in Figure 2.

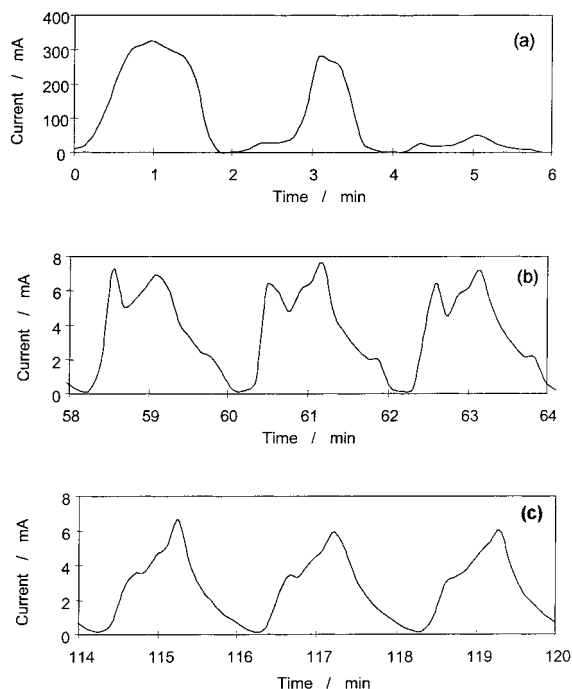


Fig. 2. Enlarged segments of the I/t response for the CPS electrolysis shown in Figure 1. (a), (b) and (c) correspond to early, middle and later stages of electrolysis. Experimental conditions have been described in Figure 1.

steel during CPS electrolysis than during the other electrolytic techniques examined. It is also apparent from the enlarged I/t diagrams that monomer reduction contributes a larger fraction of the total current during

the later stages of electrolysis than it does at the outset of the process. However, on the whole, the current tends to decrease steadily with time.

After 2 h of CPS electrolysis, a thick and uniform poly(2-vinylpyridine) coating is produced. A CSLM image of a $1\text{ mm} \times 1\text{ mm}$ portion of the coating obtained after 2 h of CPS electrolysis under the conditions described above (Fig. 3(a)) is compared with one obtained after 2 h of chronoamperometry at an applied electrode potential of -1.3 V (Fig. 3(b)). The superiority of the coating produced by CPS electrolysis is evident from the absence of craters that are present in the coatings obtained by chronoamperometric electrolysis.

3.2. Mechanism of electropolymerization coating formation

To understand the reasons for the successful coating formation by the CPS technique and the effects of the different electrolytic techniques and operating conditions on the electropolymerization process, it is important to have some knowledge of the mechanism by which poly(2-vinylpyridine) coatings are formed by electropolymerization. As with other chainwise polymerization processes, electropolymerization comprises three main steps: initiation, propagation and termination. The initiation reaction in an electropolymerization process may occur as a result of the electrochemical reduction or oxidation of species in the electrolyte to form active radicals. On the basis of earlier electro-

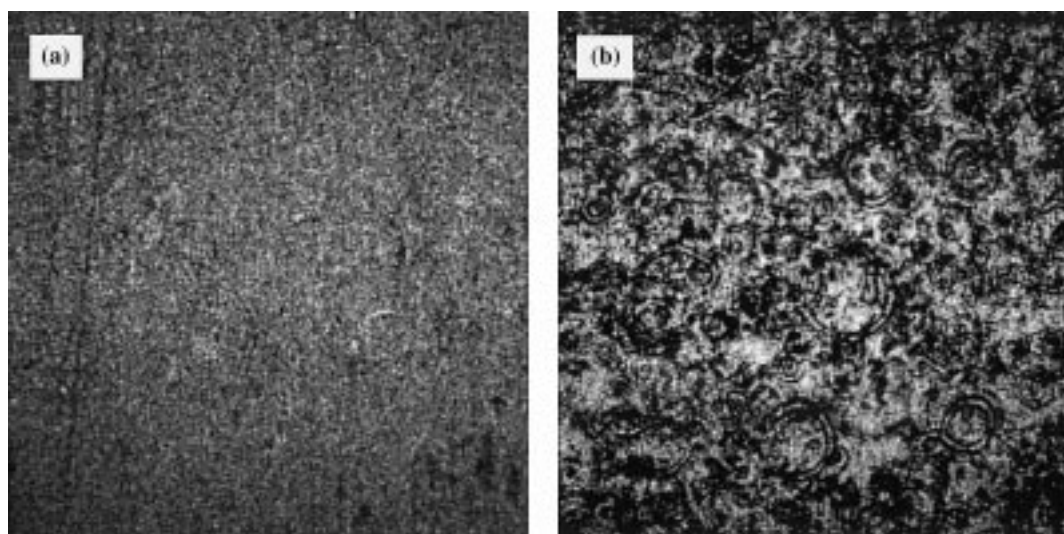


Fig. 3. CSLM images of $1\text{ mm} \times 1\text{ mm}$ portions of poly(2-vinylpyridine) coatings produced after (a) 2 h of CPS electrolysis between -0.7 and -2.5 V at a sweep rate of 30 mV s^{-1} and (b) 2 h of chronoamperometric electrolysis at -1.3 V . Other experimental conditions have been described in Figure 1.

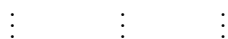
chemical and surface enhanced Raman spectroscopy studies, we have proposed the following free-radical mechanism for 2-vinylpyridine electropolymerization [10, 29]. In the pH range where good quality coatings are produced, both the neutral 2-vinylpyridine monomer (M) and the positively charged 2-vinylpyridine ion ($[H-M]^+$) coexist in the electrolyte as a result of the equilibrium:



The 2-vinylpyridine ions can adsorb onto the cathode where they are reduced during electrolysis to form $[H-M]^*$ free-radicals



These free-radicals may then combine with neutral 2-vinylpyridine molecules to initiate and propagate growing polymer chains at the cathodic surface:



where $[P_{n-1}]_{ads}^*$ and $[P_n]_{ads}^*$ represent active polymer chains growing on the electrode surface. Termination of these chains can occur via reactions with hydrogen radicals or monomer radicals also produced at the cathode or through disproportionation or combination processes.

When good quality poly(2-vinylpyridine) coatings are formed by electropolymerization, they are quite hard, adherent and insoluble in both aqueous and organic solvents. Such properties would not be expected if polymerization involved only the steps described above. Recent work [29] has suggested that a key part of the process involves the subsequent reactivation of the polymer chains once they have formed on the cathode. Similar to its monomer, poly(2-vinylpyridine) is itself basic and can be protonated in the same pH range where 2-vinylpyridine reduction and polymerization occur. Once protonated, polymer chains attached to the cathode surface may be reduced to form active polymer radical sites along their length



These pendant radicals become sites for the branching and crosslinking that give the coatings their beneficial properties described above. These radical sites may also

allow charge transport to occur within the films during electrolysis, somewhat akin to redox conduction in redox polymers [2]. This may explain why these coatings can reach thicknesses as large as 10 μm [30].

From the point of view of controlling the process, a crucial aspect of the polymerization chemistry is that reduction of the polymer chains occurs at a more negative electrode potential than that of the monomer, but tends to coincide with hydrogen evolution under typical conditions. For an electrolytic process such as conventional chronoamperometry, this creates a problem since the applied electrode potentials necessary to form a uniform and insoluble branched and cross-linked coating also lead to intense hydrogen evolution. This tends to produce a coating with a cratered morphology similar to that shown in Figure 3(b).

With this understanding of poly(2-vinylpyridine) coating formation, an explanation for the success obtained using CPS electrolysis becomes possible. Unlike chronoamperometry, CPS electrolysis varies the electrode potential over a certain range. This has an advantage because the various steps in the electropolymerization process require different electrode conditions. During each CPS cycle, the electrode potential moves from essentially open-circuit conditions to mildly cathodic and then to strongly cathodic before being reversed in the opposite direction. At mildly cathodic potentials during each cycle, monomer reduction followed by polymer chain initiation and propagation should occur. As the electrode potential reaches more negative values (less than -1.3 V), polymer chain reactivation leading to branching and/or crosslinking would begin. Although some H_2 evolution may occur during this phase, it is limited by the fact that the electrode potential remains at highly cathodic values for a very short time. Also, as shown earlier, the presence of the polymer coating itself tends to inhibit H_2 evolution. Thus, deposition of good quality films particularly during the early stages of the process suppresses H_2 evolution thereafter.

Another important stage of the process may occur when the electrode potential is close to its anodic limit and nearly open-circuit conditions prevail. During this period, almost no electron transfer reaction and, hence, no radical generation can take place. Propagation of polymer chains without electron transfer would likely predominate at these potentials. Also, while radicals are essential for initiation, they may lead to excessive termination if too many are being produced. This portion of the electrolysis may therefore help control the extent of termination relevant to that of initiation and propagation.

3.3. Effects of the potential sweep range during a CPS electrolysis

In order to obtain the best results, the potential sweep range and rate during CPS electrolysis must be adjusted appropriately. Figure 4 and Table 2 present the results obtained on the effect of the cathodic limit on coating formation for an anodic limit of -0.7 V and a scan rate of 30 mV s^{-1} . When the cathodic limit is -1.3 (Fig. 4(e)), -1.6 (Fig. 4(d)) or -1.9 V (Fig. 4(c)), only thin and non-uniform coatings form. However, by lowering the cathodic limit to -2.2 and -2.5 V (Fig. 4(b) and Fig. (a), respectively), a significant improvement is achieved and thick and uniform coatings are produced. These trends are consistent with our understanding of the electropolymerization of 2-vinylpyridine described in the previous section. When the cathodic limit is -1.9 V and more positive, the electrode potential would presumably never become negative enough for much reactivation of linear polymer chains formed as a result of monomer reduction at mildly cathodic potentials. Only by allowing the potential sweep to reach -2.2 V and below would further reduction of the existing polymer film (Equation 5) and further growth of the film be possible.

Comparison of the coating weights and current responses obtained for cathodic limits of -2.2 and -2.5 V shows very little difference. Thus, the electron transfer occurring between -2.2 and -2.5 V involves primarily hydrogen evolution and very little extra coating is produced by extending the sweep to -2.5 V. Comparison of the current responses in Figure 4 with the quality of the coatings summarized in Table 2 shows an interesting relation between the two. A thick and uniform coating tends to be associated with a response in which a very high current during the first one or two cycles is followed by a dramatic drop to a very low current thereafter. When a poor quality coating forms, the initial current is not as high and its decrease in magnitude from cycle to cycle tends to be more gradual. This difference is obviously linked to the effectiveness of

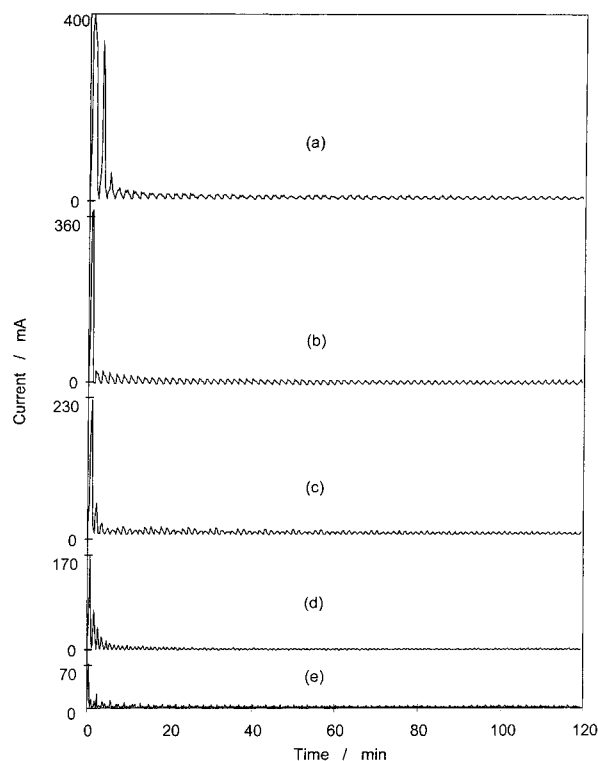


Fig. 4. Effect of the cathodic limit on the I/t response obtained during CPS electrolysis of poly(2-vinylpyridine) coatings on mild steel at a sweep rate of 30 mV s^{-1} . Solution conditions are described in Figure 1 and potential limits are given in Table 2.

a coating in increasing the resistance of the cathode to electron transfer processes. As reported, it is the first layer of polymer film that is particularly crucial in modifying the electrode properties and suppressing H_2 evolution [2–4]. This suggests that the quality of the coating can be assessed by inspection of the I/t response after only a few minutes of electrolysis.

In the next series of experiments, the anodic limit was varied while the cathodic limit was fixed at -2.2 V and the scan rate was fixed at 30 mV s^{-1} . The results shown in Figure 5 and Table 3 indicate that if the

Table 2. Effect of the cathodic limit during CPS electrolyses on coating formation for an anodic limit of -0.7 V and at 30 mV s^{-1} sweep rate

Legend in Fig. 4	Anodic limit /V	Cathodic limit /V	Coating weight /mg	Result
(a)	-0.7	-2.5	5.6	Thick and uniform coating
(b)	-0.7	-2.2	5.7	Thick and uniform coating
(c)	-0.7	-1.9	3.3	Thin and non-uniform film
(d)	-0.7	-1.6	1.6	Very thin and irregular film
(e)	-0.7	-1.3	0.3	No visible coating formed

Corresponding I/t diagrams are shown in Figure 4

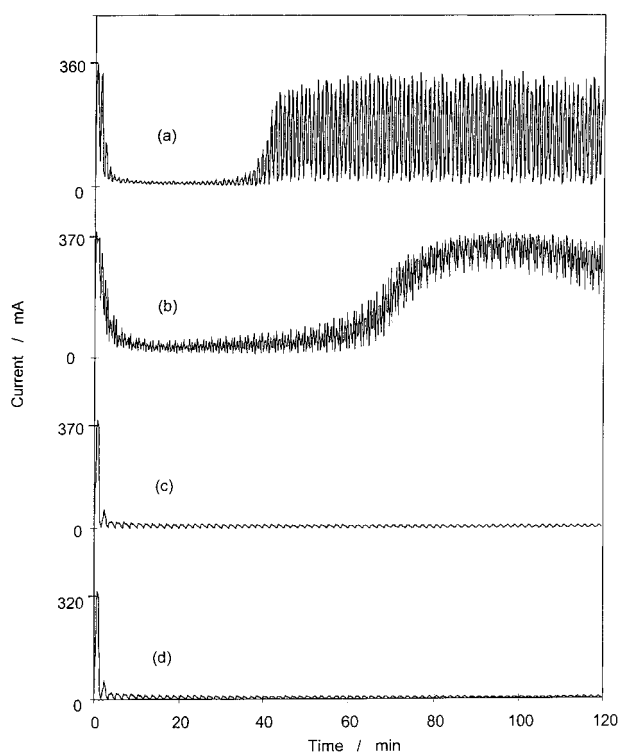


Fig. 5. Effect of the anodic limit on the I/t response obtained during CPS electrolysis of poly(2-vinylpyridine) coatings on mild steel at a sweep rate of 30 mV s^{-1} . Solution conditions are described in Figure 1 and potential limits are given in Table 3.

anodic limit is not low enough (-1.3 and -1.6 V), the resulting coatings are not only thin and non-uniform, but porous and poorly adherent as well. The current decreases to very low values in the early stages of electrolysis, although the drop is not as abrupt as is observed for the best coatings. After about 30 to 60 min, a dramatic change in the electrode response occurs. The current rise as the potential moves in the cathodic direction during each cycle increases sharply in magnitude before levelling off at a value close to what is observed at the cathodic limit in the first cycle of the electrolysis. In the case of an anodic limit of -1.6 V (Fig. 5(a)), the current still manages to drop to

relatively low values when the electrode potential reaches the anodic limit. The result is a response in which the current varies more than 300 mA over the course of each cycle. For an anodic limit of -1.3 V , the behaviour is somewhat different in that the current does not drop to low values during the anodic-going part of the scan (Fig. 5(b)). Nevertheless, the responses in both Figure 5(a) and (b) are characteristic of a process in which a protective coating forms at the outset, but is too thin and nonuniform to prevent its rupture later during electrolysis. This reactivates the mild steel surface and allows the cathodic reactions to proceed at a high rate.

The poor results obtained for these anodic limits may be explained in the following way. As suggested in the previous section, allowing the electrode potential to be more positive than -1.0 V for a period of time may be important to enable enough chain propagation, branching and crosslinking to occur. By cutting off the anodic formation at -1.6 or -1.3 V , this important part of coating formation may be excluded. As shown in Figure 5(c) and (d) and Table 3, extension of the anodic limit to -1.0 or -0.7 V will allow a uniform, protective coating to form. The results in Figure 5 show once again that the shape of the I/t response is reflective of coating quality.

3.4. Effects of the potential sweep rate during CPS electrolysis

The effect of potential scan rates between 5 and 100 mV s^{-1} have been studied for CPS between -1.0 and -2.2 V (Fig. 6 and Table 4). At a sweep rate of 100 mV s^{-1} , the current peak during the first cycle is very high (Fig. 6(a)) compared to the I/t diagrams of this series for lower potential sweep rates (Fig. 6(b) to (e)). Intense hydrogen evolution at the electrode surface is observed throughout the electrolysis and only a relatively thin and non-uniform coating is produced (Table 4). At such a high sweep rate, there may not be sufficient time for the various steps of coating formation

Table 3. Effect of the anodic limit during CPS electrolyses on coating formation for a cathodic limit of -2.2 V and at 30 mV s^{-1} sweep rate

Legend in Fig. 5	Anodic limit /V	Cathodic limit /V	Coating weight /mg	Result
(a)	-1.6	-2.2	1.7	Thin and irregular coating, porous and poorly adherent
(b)	-1.3	-2.2	1.4	Thin and irregular coating, porous and poorly adherent
(c)	-1.0	-2.2	6.6	Thick and uniform coating
(d)	-0.7	-2.2	5.7	Thick and uniform coating

Corresponding I/t diagrams are shown in Figure 5

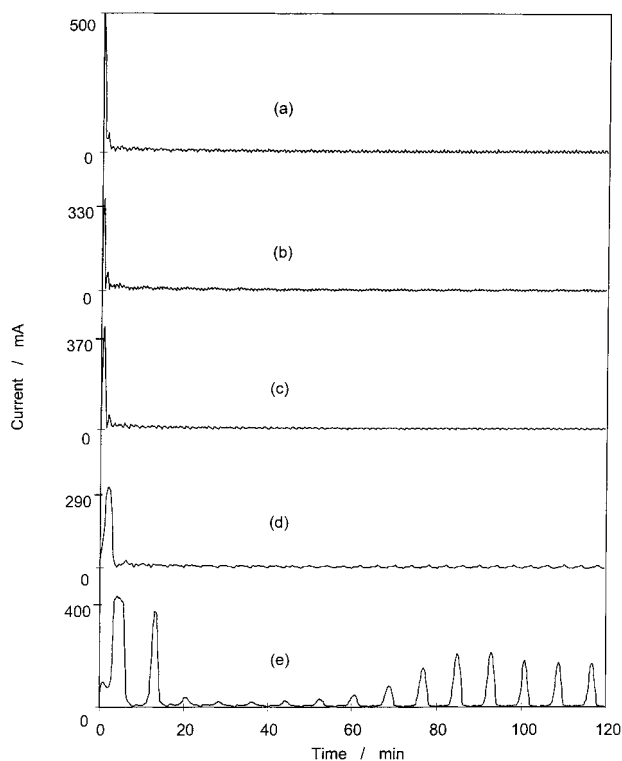


Fig. 6. Effect of the potential sweep rate on the I/t response obtained during CPS electrolysis of poly(2-vinylpyridine) coatings on mild steel. Solution conditions are described in Figure 1 and potential limits are given in Table 4.

to proceed in an optimum way. This may be particularly true once some coating has formed and if neutral 2-vinylpyridine and positive 2-vinylpyridinium ions must be transported to sites within the coating in order for further reaction to occur. At the other extreme of a low sweep rate of 5 mV s^{-1} , the coating is also nonuniform and poorly adherent. The I/t diagram (Fig. 6(e)) shows an abnormal shape. The current decreases slowly at the beginning of electrolysis, but then begins to increase after about 40 min. The current response during each cycle is characterized by a single peak at the cathodic limit. Although the electrode potential in every cycle is

now held longer at near open-circuit, mildly cathodic and strongly cathodic conditions, the period of time may be too long for polymer initiation, propagation, branching and crosslinking to cooperate effectively to form a protective coating. Only when the potential sweep rates are between 10 to 50 mV s^{-1} are coatings with acceptable quality produced. The corresponding I/t diagrams (Fig. 6(b) to (d)) are similar to each other and to those for good coatings shown in previous Figures.

4. Conclusions

The cyclic potential sweep technique has been studied for application to *in situ* polymer coating formation by electropolymerization of monomer. With a suitable combination of the potential sweep range and rate, thicker and more uniform poly(2-vinylpyridine) coatings have been formed on mild steel substrates than is possible with other electrolytic techniques. The most suitable potential range for the CPS electrolysis is found to be between -1.0 and -2.2 V vs SCE and the optimum sweep rate is between 10 and 50 mV s^{-1} . The effectiveness of the CPS technique appears to be linked to the fact that it allows the electrode potential to vary throughout the electrolysis and to be compatible with polymer initiation, propagation, branching and crosslinking that are necessary for good quality coatings to be formed. With these promising results for 2-vinylpyridine electropolymerization, further study into the application of this technique for the formation of other polymer coatings is warranted.

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Table 4. Effect of the potential sweep rate on coating formation (in the potential range of -1.0 to -2.2 V)

Legend in Fig. 6	Potential sweep rate $/\text{mV s}^{-1}$	Coating weight $/\text{mg}$	Result
(a)	100	4.9	Nonuniform coating
(b)	50	6.2	Thick and uniform coating
(c)	30	6.6	Thick and uniform coating
(d)	10	6.7	Thick and uniform coating
(e)	5	5.2	Even though coating is not very thin, it is nonuniform and poorly adherent

Corresponding I/t diagrams are shown in Figure 6

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