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Reduction of hexavalent chromium by polypyrrole deposited on different carbon substrates

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Pollution due to toxic hexavalent chromium has reached dangerous levels in some parts of the world, especially in Third World countries. This work focuses on the reduction of Cr(VI) ions in aqueous media by polypyrrole deposits on porous, high area three-dimensional carbon electrodes. Since many properties of deposited polymers are known to depend on the method of synthesis we performed the electropolymerization of pyrrole either at varying potential scan rates or at constant potential on different high area carbon materials. The deposits thus obtained were then put in contact with acidic hexavalent chromium solutions; high reduction yields were obtained (up to 80%). In addition, the possibility of repeating this cycle was studied as well as the wear resistance of these deposits. Finally, the morphology of the deposits was monitored at different stages of the process by scanning electron microscopy.

Keywords: *environmental remediation*, *hexavalent chromium*, *large area electrodes*, *polypyrrole*

1. Introduction

A number of electrochemical methods offer the possibility of transforming and/or removing polluting species from gaseous, liquid or solid environments [1–4]. In many instances, the pollutant is present at the ppm level and thus its mass transfer rate to an electrode is severely limited. The use of large area, three-dimensional electrodes alleviates this problem due to the increase in the mass transfer coefficient and a higher electron transfer area. In some cases, however, the pollutant species is not electroactive (or is kinetically slow) and direct electron transfer is not viable. Electron relays (either homogeneous or heterogeneous) can then be used to shuttle electrons to or from the electrode surface. It is in this regard that a novel application of conducting polymers has been proposed. Specifically, polypyrrole (PPy) is being considered for use in the environmental remediation arena [5–7] since it has been found that it can effectively reduce hexavalent chromium to the trivalent state (less toxic and immobilizable). This is due to its redox potential and to its ability to exchange anions with the solution. Thus, this reaction is the result of two phenomena [5, 6]: (a) a spontaneous chemical reaction between the polypyrrole and the chromate, and (b) an anion exchange produced by the electroneutrality requirement upon oxidation of the polymer, whereby an anion, A^-, must be introduced into the polymer bulk during oxidation [7, 8]. In view of public concern regarding Cr(VI) pollution [9, 10], this process is being investigated in our laboratories as a possible alternative for the reduction of chromate concentration in wastewaters from regional industries.

It is well known that many properties of conducting polymers such as the degree of crosslinking, conductivity, morphology, etc. vary with the synthesis conditions [11, 12] such as the nature of solvent [13], the electrosynthesis method [14], and the doping agent [15]. We performed an earlier study of the synthesis of PPy deposits by cyclic potential scans on glassy carbon or platinum microelectrodes and observed that the morphology and thickness of the polymeric deposits varied with scan rate and with the nature of the electrode material [16, 17]. A chronoamperometric analysis [17] revealed that the current passed during the deposition process varies considerably with scan rate, possibly due to a kinetic competition among the different reactions involved in the electropolymerization mechanism that affects the physicochemical properties of the polymer [18]. Thus, it is of importance to find the appropriate conditions for the synthesis of a deposit for specific applications. The objective of the present work is to evaluate the performance and durability of PPy deposited on three-dimensional material possessing a large area-to-volume ratio. Such deposits are obtained either by cyclic potential scans or at constant applied potential.

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2. Experimental details

Three materials were used as electrodes: two rectangular reticulated vitreous carbon (RVC) electrodes (ERG, Inc.) of 40 and 100 ppi (pores per inch), here called RVC-40 and RVC-100, respectively, and one graphite felt electrode (GFE) with 2000 ppi (Carbone Lorraine). All the electrodes were cut to an approximate external geometric area of 1 cm^2 on each side. The RVC electrodes had a thickness of 0.6 cm. The polymer deposits were obtained by performing 40 potential scan cycles at 20, 100 and 200 $mV\,s^{-1}$, from −300 to 900 mV (Ag/AgCl), with ohmic compensation. The polymeric deposits synthesized at constant potential involved the application of +900 mV for 5 min. The auxiliary electrodes were graphite rods, and a Ag/AgCl electrode was used as the reference. The electropolymerizations were carried out in solutions 0.1 M in pyrrole (Aldrich) and 0.1 M in KCl (Baker). A PAR 173 potentiostat–galvanostat was used in conjunction with a PAR 276 interface and an M270 PAR data processing unit. After each synthesis, the modified electrode was transferred to a monomer-free solution and a voltammogram was plotted to verify the formation of the polymer. The PPy deposits were then reduced at a constant potential of −0.9 V for 30 min to ensure that the polymer was in its reduced state, which allows the reduction of chromate ions as mentioned above.

The modified electrodes were then equilibrated in 0.1 M H_2SO_4. They were then contacted with 2 cm^3 aliquots of a 1 mM $K_2Cr_2O_7$ solution in 0.1 M H_2SO_4 at open circuit for 2 h. The resulting solutions were analysed for Cr(VI) by u.v.–vis. spectroscopy (Spectronic Array 3000) and for total Cr by atomic absorption spectrometry (Perkin Elmer model 3110). The percentage of Cr(VI) reduction was calculated. After contact with the chromium solutions, the condition of each polymeric deposit was monitored by performing a cyclic voltammogram in the range −0.3 to 0.9 V in 0.1 M KCl. When a given voltammogram showed that the characteristic PPy broad peak discussed below had decreased considerably (i.e. more than 90% of its initial value), then that modified electrode was discarded. The same procedure was followed if the percentage chromium reduction by a given modified electrode fell to less than 10% of the initial chromium reduction. The modified electrodes that passed the previous tests were then regenerated by reduction at the conditions specified above, and reused until noticeable degradation occurred according to the criteria just discussed. Figure 1 shows a block diagram of the experimental process. The scanning electron microscopy was performed with a Jeol (JSM-35C) microscope.

3. Results and discussion

Figure 2 shows voltammograms obtained during the synthesis of PPy deposits on GFE as a function of the number of potential scan cycles. After the 40th cycle, no significant increase in current was observed. From here, it was decided to grow all the polymeric deposits during 40 potential cycles. Figure 3 shows a typical voltammogram of polypyrrole thus synthesized on GFE and RVC electrodes at a scan rate of 20 $mV\,s^{-1}$. Two signals can be observed: an initial, extended broad wave due to the oxidation–reduction of the polymer and one at 0.9 V due to the irreversible oxidation of pyrrole. Figures 4 and 5 show the voltammograms obtained with PPy deposits synthesized under different conditions. Different amounts of polymer are deposited according to the substrate electrode and the potential scan rates utilized for the synthesis, as can be deduced from a qualitative inspection of the areas under these curves. It can be seen that more charge is passed (and thus more material is grown) when graphite felts are used, as compared to the RVC. Likewise, more charge is passed when the potential is scanned slowly (20 $mV\,s^{-1}$) than at faster rates (e.g., 200 $mV\,s^{-1}$). The deposits are known to have different thickness according to the potential scan rates utilized for their synthesis (i.e., 20, 50, 100 and 200 $mV\,s^{-1}$ [16, 17].

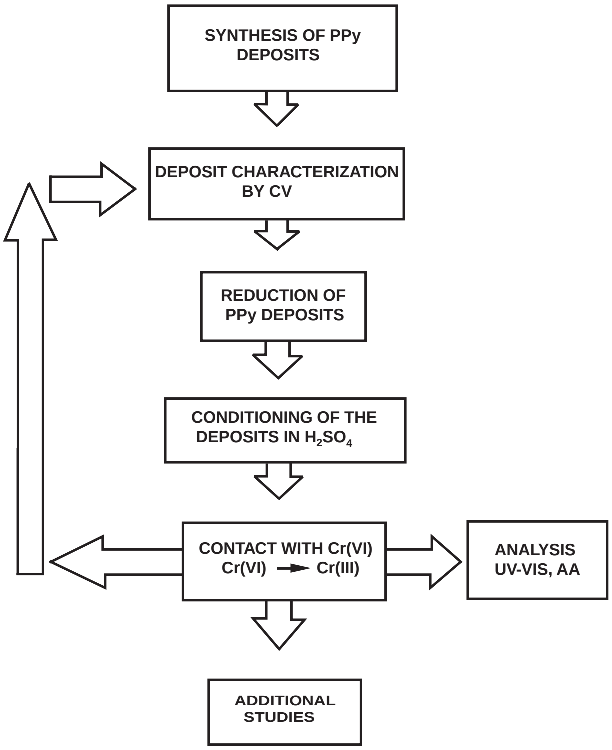

Fig. 1. Schematic diagram of the experimental process.

The results obtained with PPy deposits after the first contact with the chromium(VI) solutions are shown in Fig. 6A, where the percentage of chromium (VI) reduction is reported. The polymer deposited on the three materials at 20 $mV\,s^{-1}$ yields significantly better results than the others (i.e. almost 80% Cr(VI) reduction). Likewise, the PPy obtained at constant potential on GFE also shows high reduction yields (77%). Figure 6B shows the results obtained with these same polymeric deposits (upon regeneration, as

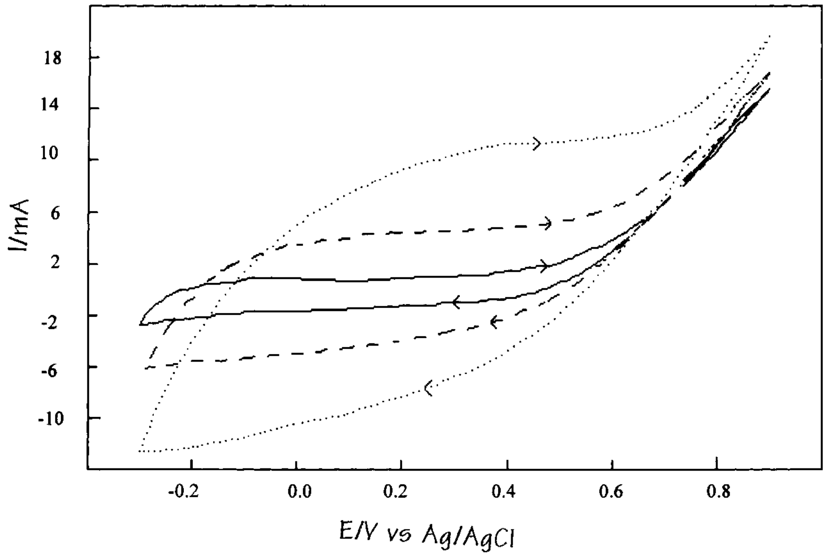

Fig. 2. Voltammograms obtained during the synthesis of PPy deposits on GFE as a function of the number of potential scan cycles. Scan rate 20 mV s^{-1}. Cycle 1 (——), Cycle 25 (- - - -) and cycle 40 (· · · ·).

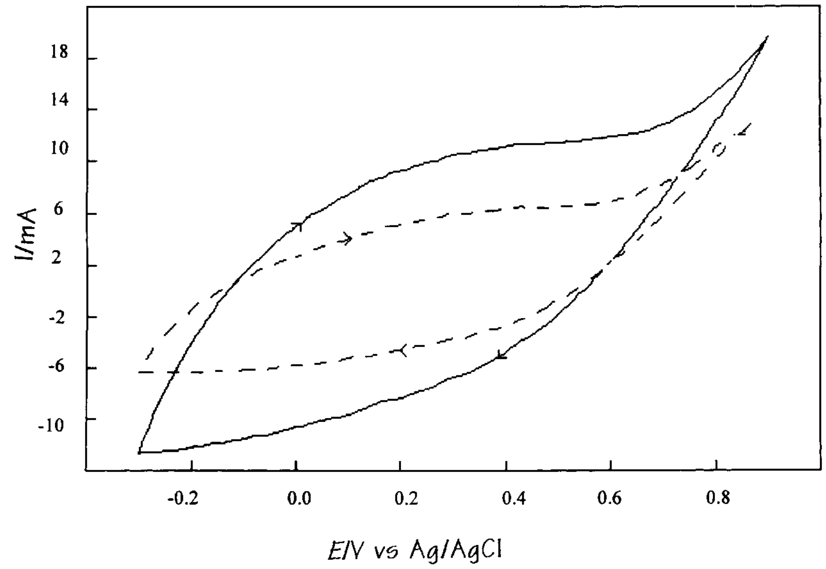

Fig. 3. Voltammogram of PPy synthesized after 40 potential scan cycles (at 20 mV s^{-1}) on a graphite felt electrode (GFE) (——) and on a reticulated vitreous carbon electrode (RVC, 100 ppi) (- - - -). Scan rate 20 mV s^{-1}.

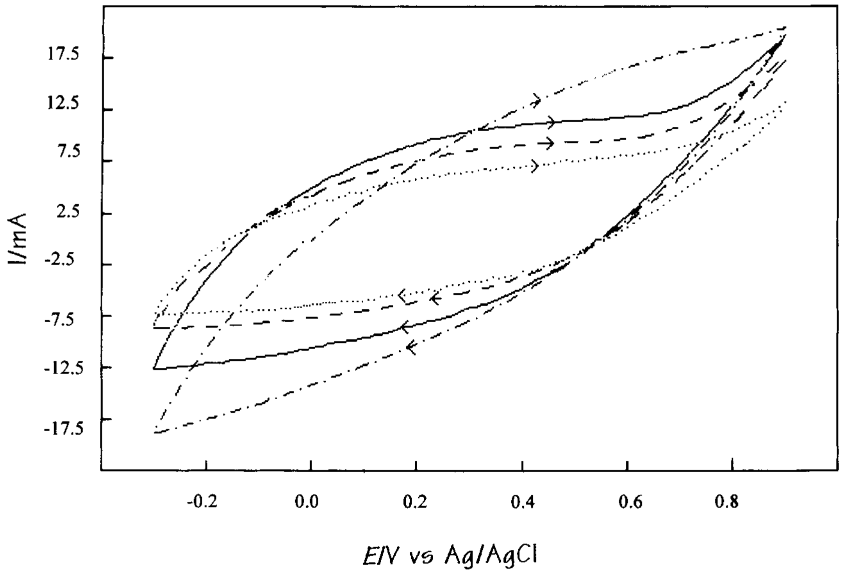

Fig. 4. Voltammogram of PPy synthesized after 40 potential scan cycles (at 20 (——), 100 (- - - -) and 200 (· · · · ·) mV s^{-1}) or else at a constant potential of −0.9 V (— · —) (vs Ag/AgCl) for 5 min on a graphite felt electrode (GFE). Scan rate 20 mV s^{-1}.

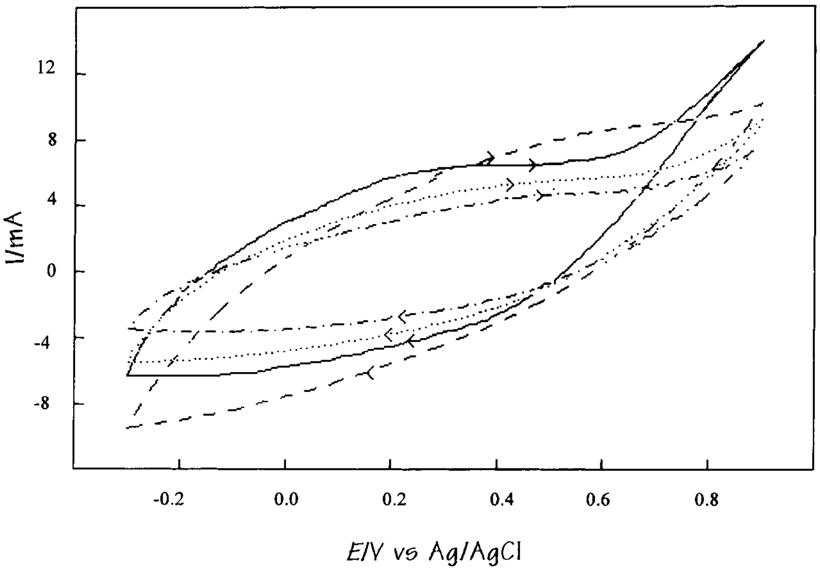

Fig. 5. Voltammogram of PPy synthesized after 40 potential scan cycles (at 20 (——), 100 (·····) and 200 (— · —·) mV s^{-1}) or else at a constant potential of −0.9 V (- - -) (vs Ag/AgCl) for 5 min on a reticulated vitreous carbon electrode (RVC, 100 ppi). Scan rate 20 mV s^{-1}.

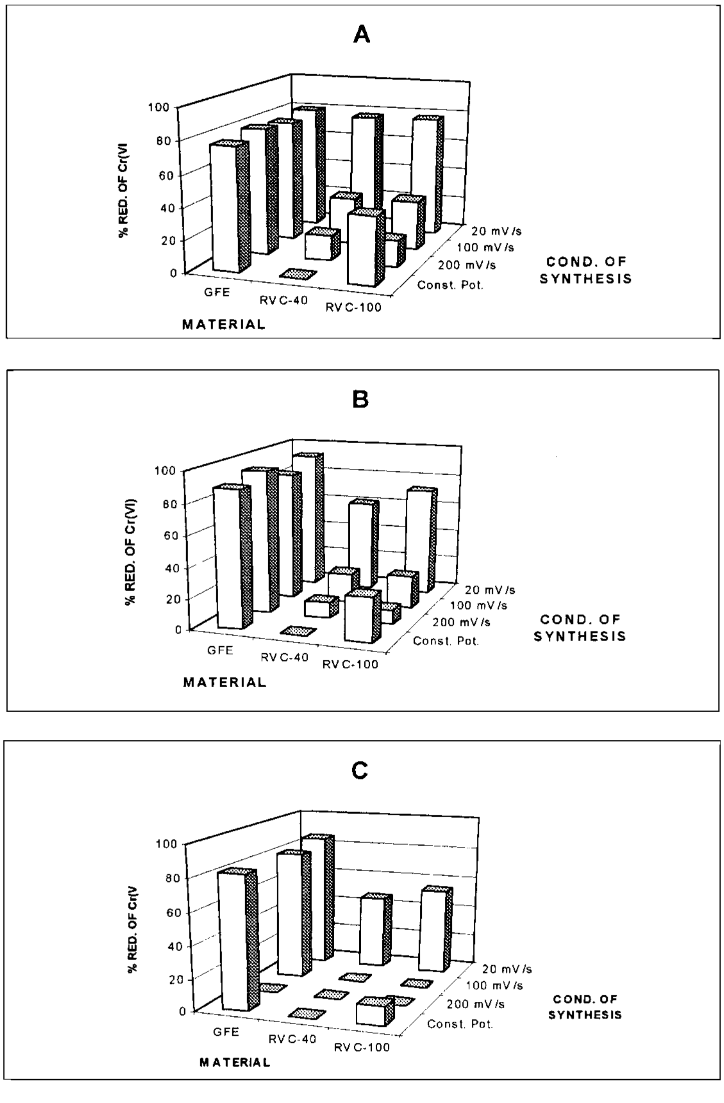

Fig. 6. Percentage of chromium reduction after immersion of the PPy deposits (synthesized under different conditions of potential as shown) in 2 cm^3 of a 1 mM $K_2Cr_2O_7$ solution in 0.1 M H_2SO_4 for two hours: (A) first cycle, (B) third cycle, (C) sixth cycle.

described above) after a third contact with unused chromium solutions. The percentage reductions obtained with the polymeric deposits on graphite felt remain high, whereas those obtained with the RVC decrease considerably. Figure 6C shows the results after the sixth contact with the same polymeric deposits. Again, the deposits on the felt yield the highest conversions and appear to be the most resistant to degradation, even after the 9th cycle (not shown here) where the percentage reduction is 75%, whereas the others decrease considerably and, in some cases, become negligible. From these data it is clear that the method of synthesis, as well as the substrate material, determine the types of results obtained. That is, PPy grown on GFE is more resistant to degradation and to the loss of redox properties than that grown on RVC. The same observations apply to the PPy deposits grown on RVC at a slow potential scan rate ($20\,\mathrm{mV\,s^{-1}}$) as compared to those grown either at a constant potential or at scan rates higher than this. The loss in current response after successive contact cycles with chromium solutions is shown in Fig. 7 for PPy grown as described above on GFE. The initial open circuit potential of PPy grown by potential scans at 100 mV $\mathrm{s^{-1}}$ (as described earlier) was 755 mV in the chromate solution. This potential was measured again after two hours of contact with this solution and was found to be 830 mV. Likewise, the initial open circuit potential of PPy grown at a constant potential (as described earlier) was 715 mV; after two hours, it was 885 mV. Since the chromate solution has been reduced to chromium (III), these potentials indicate that the PPy has been oxidized by the chromate.

In an attempt to correlate the physical condition of the PPy deposits with the above results, they were oberved by scanning electron microscopy (SEM) and the results are shown in Fig. 8(a–f). The substrate materials are shown in Fig. 8(a) (GFE) and 8(d) (RVC). The polymeric deposits (before contact with the chromate solutions) are shown in Fig. 8(b) (on GFE) and 8(e) (on RVC), whereas those after six contact cycles are shown in Fig. 8(c) (on GFE) and 8(f) (on RVC). All these deposits were obtained at $100\,\mathrm{mV\,s^{-1}}$. By comparing Fig. 8(b) and 8(e), the type of growth on GFE and RVC is different (small grains on GFE and large ‘chunks’ on RVC). Evidence of the type of PPy loss from the electrodes is given in Fig. 8(c) and 8(f). On GFE, PPy deposits dislodge as a crust, whereas on RVC the large ‘chunks’ show a gradual loss of material. These observations agree well with those discussed above. At least in the case of GFE, a strategy for obtaining PPy deposits more adherent to the substrate would most likely yield significantly better results in terms of durability. In addition, under the conditions described in the present work, PPy deposits on RVC occur fundamentally on the outer layers (see Fig. 9) which precludes the possibility of obtaining better results by using forced flow through the porous material. Likewise, high pressure drops derived from the use of GFE call for a redesign of the present experimental system. We are currently studying suitable conditions (nature and composition of the synthetic electrolytic medium, applied potential, regeneration time, etc.) with the aim of achieving a continuous process.

4. Conclusions

We have obtained polypyrrole deposits on three dimensional, carbon based electrodes. PPy deposits on graphite felts show greater efficiency and cycleability for the reduction of hexavalent chromium than those on RVC. This may be attributed to the larger amount of polymer deposited on the former. In addition, the method of synthesis determines the final characteristics of the deposit. For example, the deposits obtained by potential scan cycles at $20\,\mathrm{mV\,s^{-1}}$ showed

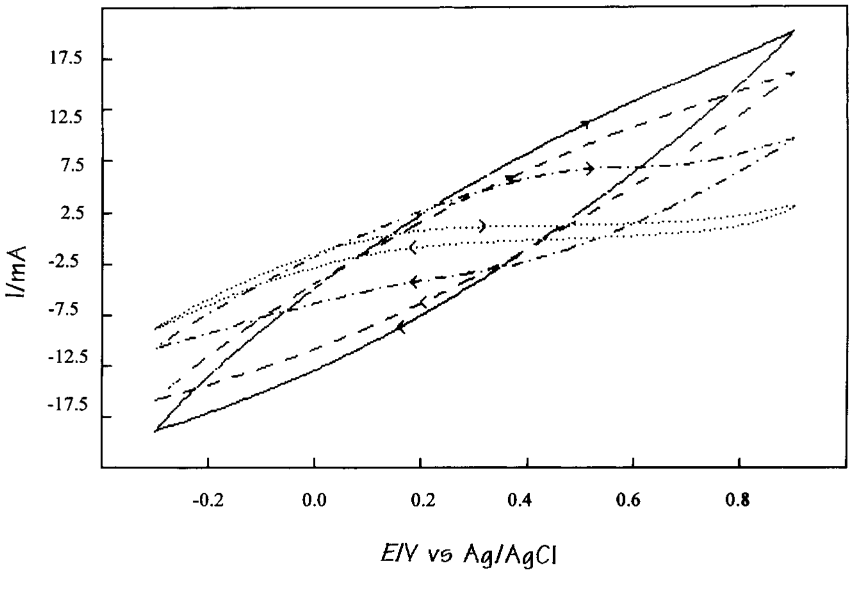

Fig. 7. Voltammograms after successive contact cycles with chromium solutions for PPy grown on GFE at $20\,\mathrm{mV\,s^{-1}}$. Initial contact (—), contact 2 (- - - -), contact 6 (– · –) and contact 9 (· · · · ·).

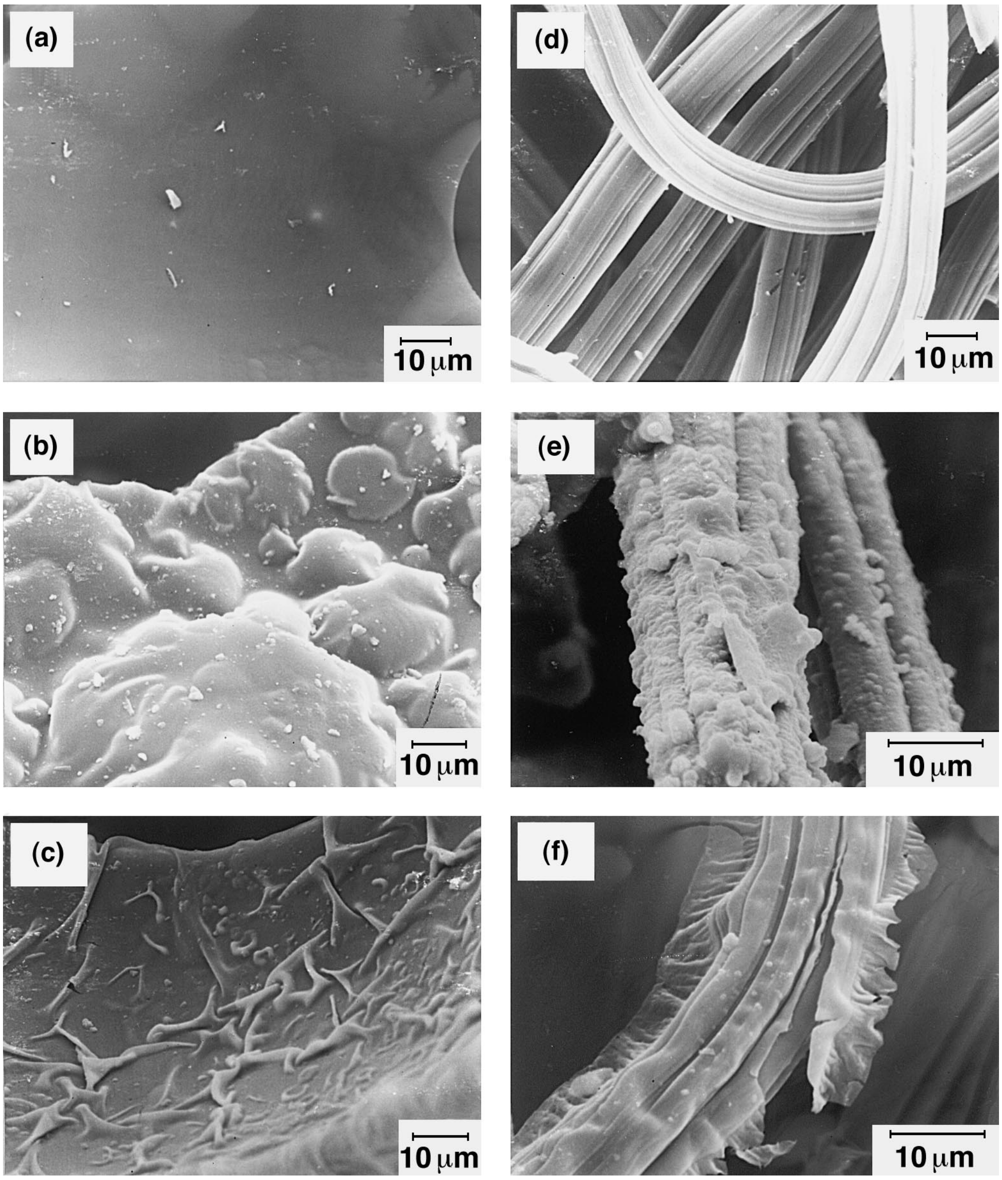

Fig. 8. Scanning electron micrographs. Amplification is 750× for samples on GFE, and 1500× for samples on 100 ppi RVC. Substrate materials are shown in A (GFE) and D (RVC). Polymeric deposits before contact with chromate solutions are shown in B (on GFE) and E (on RVC). PPy deposits after 6 contact cycles are shown in C (on GFE) and F (on RVC). All these deposits were obtained at 100 mV s^{-1}.

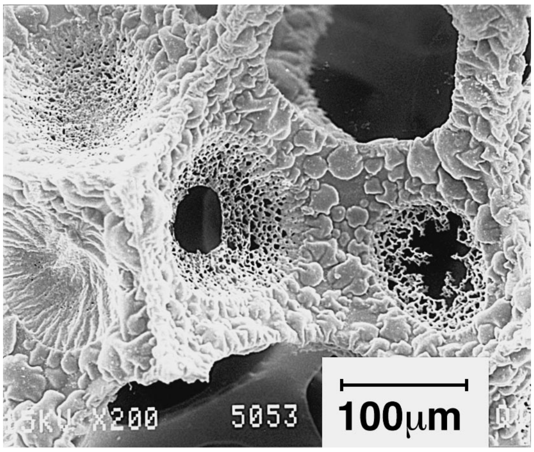

Fig. 9. Scanning electron micrograph (at 150×) of PPy grown on 100 ppi RVC at 20 mV s^{-1}.

better results in terms of percentage chromium reduction, as well as cycleability than the others. This may be due to the facilitation of the kinetics of one or more of the reactions involved in the electropolymerization mechanism yielding more compact and adherent deposits on the substrate material.

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