Journal of Applied Electrochemistry **34**: 1259–1263, 2004.

Reaction rate and electrochemical stability of conducting polymer films used for the reduction of hexavalent chromium

L.A.M. RUOTOLO*, A.A. LIAO and J.C. GUBULIN
Department of Chemical Engineering, Federal University of São Carlos, P.O. Box 676, 13565-905 São Carlos, SP, Brazil
*(*author for correspondence, e-mail: luis_ruotolo@hotmail.com)*

Received 26 February 2004; accepted in revised form 13 July 2004

Key words: Cr(VI), effluent treatment, polyaniline, polypyrrole, reticulated vitreous carbon (RVC)

Abstract

The reduction of toxic hexavalent chromium to its trivalent state at conducting polymers films was studied. The process is based on the capacity of conducting polymers to spontaneously donate electrons to the Cr(VI) species. Electrodes of polyaniline and polypyrrole, deposited as films on reticulated vitreous carbon (RVC), were prepared. The process of Cr(VI) reduction was studied under open and closed circuit conditions. It was observed that polyaniline was only suitable for use only under closed circuit conditions, whereas polypyrrole did not perform well under either open or closed circuit conditions. The electrocatalytic power of polyaniline for Cr(VI) reduction was demonstrated when the reaction rates for bare RVC and RVC/PANI were compared.

1. Introduction

Hexavalent chromium (Cr(VI)) is highly toxic, not only to humans but also to aquatic life [1]. Wastes containing Cr(VI) are generated by a large variety of industrial activities such as metal finishing, dying and metallurgy to name only a few. Because of this Cr(VI) is widely encountered in industrial waste discharges. In view of these facts, the Brazilian government established a maximum limit of 0.1 mg dm^{-3} of Cr(VI) in industrial effluents to be discharged into water courses.

In nature Chromium is most commonly found in the Cr(III) and Cr(VI) oxidation states. Compounds of Cr(III) are reported as being 10–100 times less toxic than those of Cr(VI). Also, whereas Cr(VI) is highly mobile in the environment, Cr(III) is easily precipitated or adsorbed on a variety of inorganic and organic substrates [2]. Traditional techniques for removing Cr(VI) from industrial wastes generally involve two steps; (i) Cr(VI) is chemically reduced to Cr(III) using a suitable reducing agent (e.g., SO_2, $FeSO_4$) followed by, (ii) precipitation of Cr(III) in the form of $Cr(OH)_3$ using lime or NaOH. The development of new technologies to improve or substitute the above conventional process is both economically and environmentally desirable. Several alternatives have been studied, for example, studies using adsorptive [3, 4], photochemical [5] and electrochemical [6, 7] processes can be found in the literature. Among the electrochemical processes, the direct electroreduction of Cr(VI) been attempted at carbon substrates such as reticulated vitreous carbon (RVC) [8]. However, this process is economically unfavourable because of the low reaction rates and current efficiencies obtained. In an attempt to solve this problem, indirect reduction employing a redox mediator such as Fe^{2+}/Fe^{3+} was proposed. This process is very efficient and with progress in membrane technology, offers promise of implementation [8].

Processes using conducting polymer films, deposited on substrates with large surface areas, eliminate the necessity of a separation step, as in the Fe^{2+}/Fe^{3+} process. Among the various applications of conducting polymers, their use in a chemical process for Cr(VI) reduction has been discussed [2, 8]. This process is based on the spontaneous electron transfer from the polymer to the Cr(VI) present in dilute acid solutions. The conducting polymer most commonly studied for this process is polypyrrole under open circuit conditions, but degradation problems and decrease in the ability to reduce Cr(VI) after some cycles have been reported [8, 9].

A spectrophotometric study using polyaniline for the reduction of Cr(VI) showed that the contact of the polyaniline film with Cr(VI) solution under open circuit potential had the same effect of keeping it under very positive potentials where polymer degradation (polyaniline hydrolysis) takes place [10, 11]. An attempt to stabilise polyaniline against its electrochemical degradation using a large polyanion dopant failed. Only indigotetrasulfonate (ITS) stabilises PANI to some extent at high electrode potential [12]. Under controlled potential conditions Malinauskas and Holze [10] observed that Cr(VI) reduction was independent on the cathodic potential imposed. From their results they deduced the following reaction sequence. Leucoemeraldine form of PANI was oxidised by chromium VI. By applying an electrode potential of 0.2 V vs RHE PANI film is reduced to its initial leucoemeraldine form. As a result, a net electroreduction of Cr(VI) takes place and PANI film acts as an electrocatalyst in this reaction sequence. They concluded that the chemical redox reaction between Cr(VI) and PANI was the rate-determining step, whereas the cathodic reduction of PANI film proceeded relatively fast. This conclusion coincided with the one obtained by Wang and Rajeshwar in their electrochemical study of Cr(VI) reduction using a polypyrrole/glassy carbon electrode [13].

Ruotolo and Gubulin [14] studied the effect of film thickness, potential and flow velocity on the reaction rate of Cr(VI) reduction at PANI/RVC in a flow cell. They observed a potential independence of the reaction rate with the flow velocity and film thickness and concluded that the mass transfer was the rate-limiting step of the process and that the reaction occurred on the outside of the polymer layer.

More recently, the synergistic interactions in a polypyrrole-coated aluminium electrode was studied by Conroy and Breslin [15]. They observed that the catalyst functioned with a self-sustained regeneration mechanism in which Cr(VI) was reduced by PPY^0 to generate PPY^+, but the PPY^+ was subsequently reduced to PPY^0 by oxidation of the aluminium substrate. The authors also observed a current reduction in voltammograms taken after some cycles and concluded that this reduction could be connected with polypyrrole degradation or with aluminium oxide formation.

In this work, the ability of RVC, polypyrrole and polyaniline to reduce Cr(VI) to Cr(III) in a flow cell was investigated and compared. Two different operating conditions were studied: open and closed circuit conditions. The reaction rate and the stability of the conducting polymer were evaluated.

2. Experimental

The reduction of Cr(VI) was performed in a flow cell (Figure 1). The working electrode/cathode was a 60 ppi RVC (Electrosynthesis Company) 3D mesh (0.7 cm × 1.0 cm × 3.0 cm) coated with either polyaniline (PANI) or polypyrrole (PPY) films. A vitreous carbon plate was connected to the cathode to act as a current feeder. The counter electrode/anode was a Ti/RuO_2 DSA® plate (De Nora). A polyethylene mesh, covered with a polyamide fabric, was positioned between the anode and the cathode in order to avoid short circuits.

Potential control was achieved using an Autolab PGSTAT30 potentiostat (Eco Chemie). All the potentials are referred to Ag/AgCl 3.0 M KCl reference electrode (207 mV vs standard hydrogen electrode (SHE)). The concentration of Cr(VI) was continuously measured at a wavelength of 350 nm using an ULTROSPEC 2100pro UV–vis spectrophotometer from Amersham Pharmacia Biotech.

The porous cathode was coated with a thin film of potentiodynamically deposited conducting polymer. Polypyrrole was deposited from a solution of 0.1 M pyrrole and 0.1 M K_2SO_4 in the potential range of −0.2 to 0.8 V at a sweep rate of 100 mV s^{-1} [16]. Polypyrrole film was grown for 40 cycles. Polyaniline was deposited from a solution of 0.1 M aniline and 1.0 M H_2SO_4 in the potential range of −0.1 to 0.8 V at a sweep rate of 50 mV s^{-1} [17]. All the polyaniline film electro-syntheses were performed until a current peak of 14 mA was reached. In order to eliminate monomer and oligomer residues, immediately after preparation the polymer films were washed and their electrochemical responses

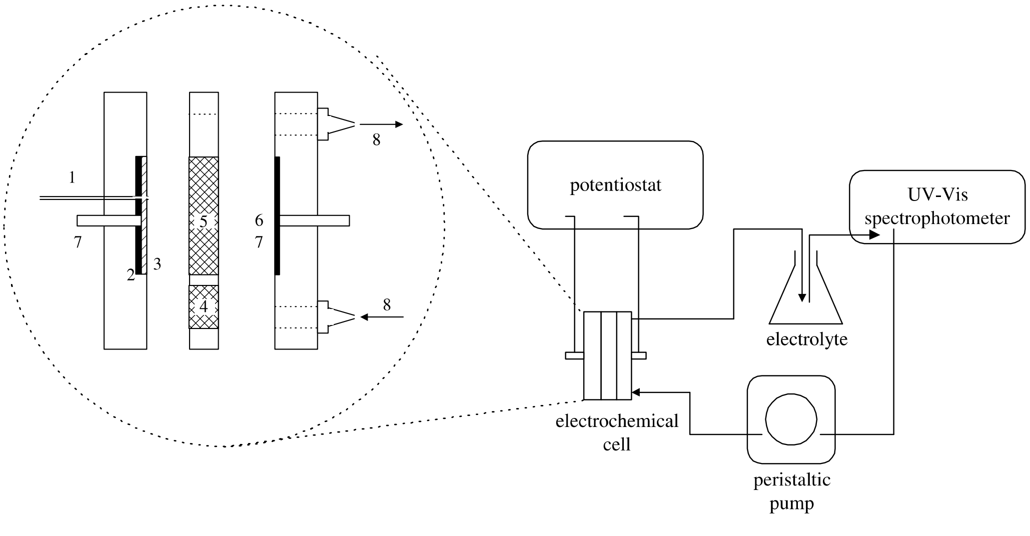

Fig. 1. Equipment and electrochemical cell. (1) Luggin capillary; (2) counter electrode; (3) separator; (4) flow distributor; (5) porous cathode; (6) current feeder; (7) electrical contacts; (8) electrolyte inlet and outlet.

recorded at a sweep rate of 50 mV s^{-1} in 0.1 M K_2SO_4 for polypyrrole and 0.5 M H_2SO_4 for polyaniline.

The process of Cr(VI) reduction was initiated, immediately after the electrochemical response of the film had been recorded. In the experiments performed under open circuit conditions, the peristaltic pump was turned on and the solution absorbance was recorded as a function of time. In the experiments carried under closed circuit conditions, in order to avoid the contact of the conducting polymer with the Cr(VI) solution under open circuit conditions, the potential was applied before the peristaltic pump (with the flow velocity previously adjusted) was turned on. All the experiments were performed using a flow velocity of 13.0×10^{-3} m s^{-1}. At the end of each run the electrolyte was removed from the cell and the electrochemical response of the film was recorded in 0.1 M K_2SO_4 (polypyrrole) or 0.5 M H_2SO_4 (polyaniline) as described previously. The comparison of the voltammograms before and after the reaction with Cr(VI) permitted an evaluation of the polymer stability.

An electrolyte volume of 0.05 dm^3 0.1 M H_2SO_4 containing 40 or 100 mg dm^{-3} Cr(VI) was used in the electroreduction studies. The Cr(VI) source was potassium dichromate. All reagents used were of analytical grade and all the solutions were prepared using deionised water. Aniline and pyrrole monomers were distilled under vacuum before use. The electrolyte temperature was maintained in the range of 25–28 °C.

3. Results and discussion

The results of Cr(VI) reduction carried out under open and closed circuit conditions are shown in Figures 2 and 3, respectively. The values of potential for polypyrrole were chosen based on the relevant literature [13]. The potential of −0.05 V is slightly more negative than the PPY redox potential and the other two potentials were chosen in order to compare with the polyaniline results. The range of potentials studied for polyaniline was chosen in order to avoid its degradation (potentials lower than 0.6 V) and to study the effect of its oxidation state. At −0.2 V PANI is fully reduced (leucoemeraldine state) and at 0.2 V PANI is partially reduced and in its most conductive state (emeraldine).

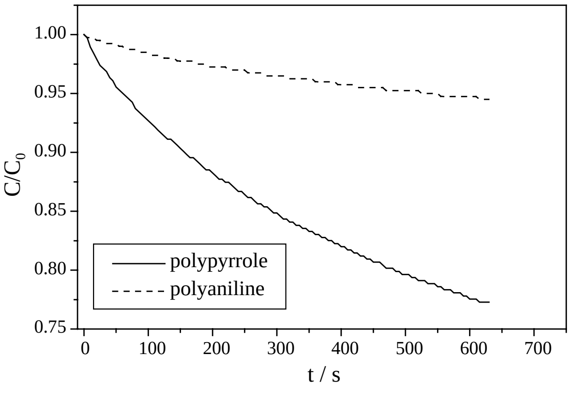

Fig. 2. Normalised Cr(VI) concentration depletion as a function of time. Process carried out under open circuit conditions. Initial concentration: 40 mg dm^{-3}.

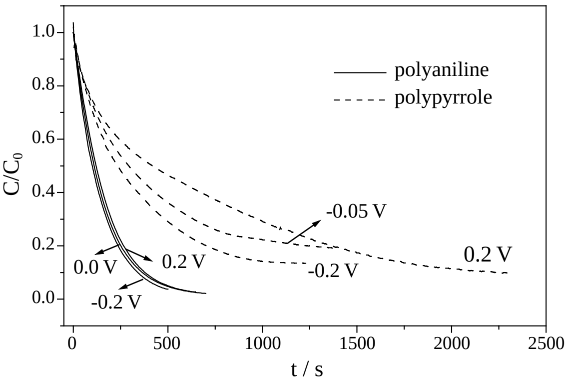

Fig. 3. Normalised concentration depletion as a function of time. Process carried under closed circuit conditions. Initial concentration: 40 mg dm^{-3}.

At open circuit condition the reaction rate observed when using polypyrrole films is much greater than that for polyaniline films. Polypyrrole is also much more stable than polyaniline (Figure 4 (a) and (b)). Despite this, a small loss of electrochemical activity for polypyrrole occurs, as confirmed by the reduction of the current peak at approximately 0.4 V in Figure 4(a). This behaviour is not acceptable when several successive electroreduction cycles are to be performed. In fact, some authors [8, 9, 18] have observed the loss of the polypyrrole activity for Cr(VI) reduction after a number of cycles and this has been attributed to possible degradation reactions occurring in the polymer film.

Polyaniline is not suitable for use under open circuit conditions due to the fact that it degrades at potentials higher than 0.6 V vs SCE [19]. This is illustrated in Figure 4(b), where the effect of electroreduction of Cr(VI) at ployaniline films under open circuit conditions is manifested by the deactivation (degradation) of the polymer film. Potentials recorded under open circuit conditions during the reaction showed values of approximately 0.7 V vs Ag/AgCl. Thus, this explains why the process does not work for polyaniline under the conditions used. The main degradation product, detected by UV–vis and cyclic voltammetry, was benzoquinone, which is in agreement with the literature [19–21].

In order to improve the electrochemical stability of the conducting polymers during the Cr(VI) reduction process a more cathodic potential than that of the open circuit potential was applied to the film in order to avoid the anodic potentials at which the polymer degrades. These experiments, carried under closed circuit conditions, are shown in Figure 3. Although polypyrrole shows faster kinetics than observed under open circuit conditions, this kind of cathodic protection was not effective in maintaining the stability of the polypyrrole, as can be seen in Figure 4(c). PPY presented both slower

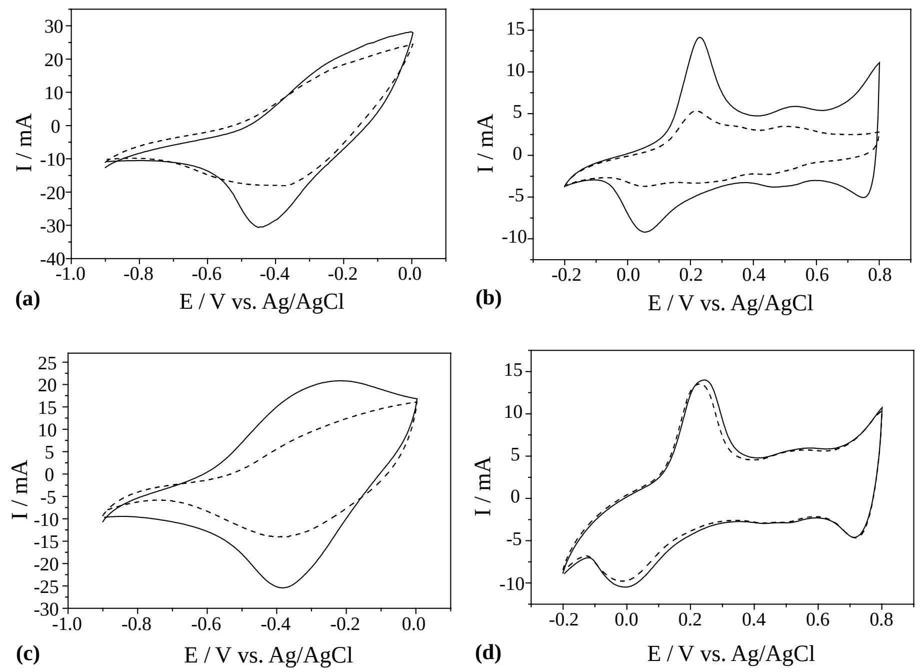

Fig. 4. Electrochemical responses. Polypyrrole (a) and polyaniline film (b) after open circuit experiments; (c) polypyrrole film after an applied potential of −0.05 V; (d) polyaniline film after applied potential of 0.0 V. (——) Before reaction with Cr(VI), (-----) after reaction with Cr(VI). Cyclic voltammograms recorded in 0.1 M K_2SO_4 for PPY and in 0.5 M H_2SO_4 for PANI, both with at a sweep rate of 50 mV s^{-1}.

reaction rates and lower electrochemical stability when compared to the polyaniline. On the other hand, the reaction rates for polyaniline were rapid and independent of the applied potential within the range studied, i.e., the reaction is mass transfer controlled. The mass transfer coefficient, k_m,was calculated adjusting the experimental curves from Figure 3 to Equation 1, which was deduced using the current limit condition:

$$\frac{C}{C_0} = \exp\left(\frac{k_m A}{V_e}\right) \tag{1}$$

where A is the electrode area (given by the RVC manufacturer); C, the bulk molar concentration of Cr(VI); C_0, the initial concentration (C_0=40 mg dm^{-3}) and V_e, the electrolyte volume (0.05 dm^3). The calculated k_m for the flow velocity used was 3.9×10^{-5} m s^{-1}. The polyaniline films remain stable after reaction with Cr(VI), as can be seen in Figure 4(d).

Comparing two different conditions under which both polypyrrole and polyaniline are stable (Figure 5), it can be observed that polyaniline under closed circuit conditions displays a faster reaction rate than that observed using a polypyrrole film under open circuit conditions. So, even though polypyrrole degradation can be eliminated [18], the use of polyaniline films remains much more attractive for industrial applications because of its higher reaction rates and stability under closed circuit conditions.

Finally, the performance of bare RVC and polyaniline coated RVC was compared. In these experiments, shown in Figure 6, a 0.1 dm^3 solution containing 100 mg dm^{-3} of Cr(VI) was used. The process was initially kinetically

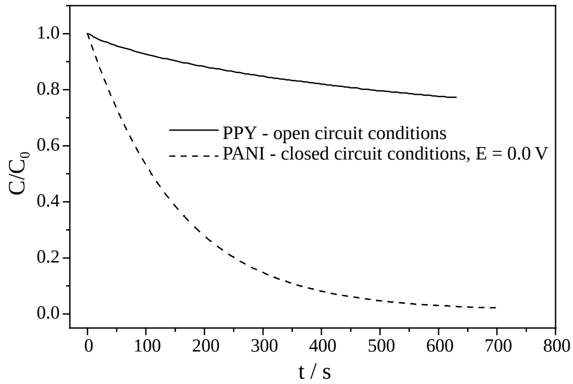

Fig. 5. Normalised concentration depletion as a function of time. Initial concentration: 40 mg dm^{-3}.

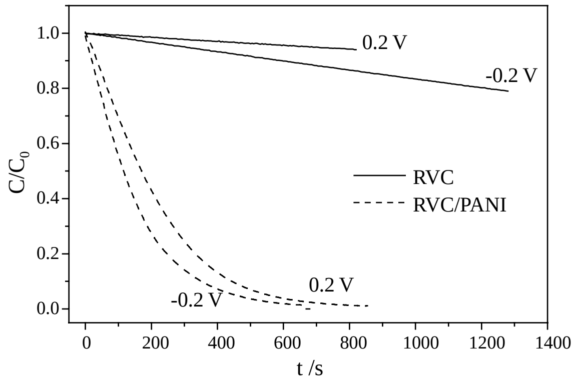

Fig. 6. Normalised concentration depletion as a function of time for bare RVC and PANI covered RVC. Initial concentration: 100 mg dm^{-3}.

controlled and, for polyaniline, the reaction rates are constant up to a transition concentration (C^*). The transition concentrations for -0.2 and 0.2 V are, respectively, 55 and 47 mg dm^{-3}, so, the greater the potential, the smaller the value of C^*. After C^* the reaction rate becomes dependent on the Cr(VI) concentration, i.e., the mass transfer starts to influence the kinetic process.

The rate constants were determined only considering the linear section of the curves shown in Figure 6. The reaction rates for the bare RVC electrodes are 1.65×10^{-3} mg s^{-1} (-0.2 V) and 7.21×10^{-4} mg s^{-1} (0.2 V) and for polyaniline covered RVC electrodes they are 0.044 mg s^{-1} (-0.2 V) and 0.030 mg s^{-1} (0.2 V). The reaction rates for the RVC/PANI electrode are much higher than those observed for the bare RVC electrodes. In this light, despite the increase in surface area provided by the polyaniline film, PANI can be considered a powerful electrocatalyst for Cr(VI) reduction. The more cathodic the potential, the faster the reaction rates, but no influence on the polymer stability was observed in the range of potential studied.

In all experiments using polyaniline films under closed circuit conditions no Cr(VI) was detected using the diphenylcarbazide (DPC) colourimetric method [22]. As the detection limit for DPC is in the range of a few ppb's (parts per billion) it was concluded that the Cr(VI) concentration was much lower than that established by the Brazilian government (0.1 mg dm^{-3}). Solution analysis by atomic absorption spectrophotometry also revealed that the total chromium concentration was unchanged.

4. Conclusions

Polypyrrole is not suitable for use in Cr(VI) reduction on an industrial scale because it is not totally stable under the conditions employed, even at low concentrations and under closed circuit conditions. Even though progress has been made in improving polypyrrole stability, the use of polyaniline proved to be more attractive because it is very efficient for Cr(VI) reduction, resulting in higher reaction rates and remaining stable when the process is carried under closed circuit conditions. Under open circuit conditions, a degradation reaction destroys the polyaniline film. As the polyaniline greatly improves the reaction rate of Cr(VI) reduction, it can be considered a powerful electrocatalyst material for the reduction of Cr(VI).

Acknowledgement

This work was financed by FAPESP (São Paulo State Research Aid Foundation, Brazil) under Project Number 99/10.822-9.

References

1. D.E. Kimbrough, Y. Cohen, A.M. Winer, L. Creelman and C. Mabuni, *Critical Rev. Environ. Sci. Tech.* **29** (1999) 1.
2. C. Wei, S. German, S. Basak and K. Rajeshwar, *J. Electrochem. Soc.* **140** (1993) L60.
3. M.P. Candela, J.M.M. Martinez and R.T. Maciá, *Wat. Res.* **29** (1995) 2174.
4. D. Petruzzelli, R. Passino and G. Tiravanti, *Ind. Eng. Chem. Res.* **34** (1995) 2612.
5. W.Y. Lin, C. Wei and K. Rajeshwar, *J. Electrochem. Soc.* **140** (1993), 2477.
6. S. Goeringer, N.R. Tacconi, C.R. Chenthamarakshan and K. Rajeshwar, *J. Appl. Electrochem.* **30** (2000) 891.
7. K.N. Njau and L.J.J. Janssen, *J. Appl. Electrochem.* **29** (1999) 411.
8. R. Senthurchelvan, Y. Wang, S. Basak and K. Rajeshwar, *Electrochem. Soc.* **143** (1996) 44.
9. M.A. Alatorre, S. Gutiérrez, U. Páramo and J.G. Ibañez, *J. Appl. Electrochem.* **28** (1998) 551.
10. A. Malinauskas and R. Holze, *Ber. Bunsenges. Phys. Chem.* **102** (1998) 982.
11. A. Malinauskas and R. Holze, *J. Appl. Pol. Sci.* **73** (1999) 287.
12. R. Mazeikiene and A. Malinauskas, *Eur. Pol. J.* **38** (2002) 1947.
13. Y. Wang and K. Rajeshwar, *J. Electroanal. Chem.* **425** (1997) 183.
14. L.A.M. Ruotolo and J.C. Gubulin, *J. Appl. Electrochem.* **33** (2003) 1217.
15. K.G. Conroy and C.B. Breslin, *J. Appl. Electrochem.* **34** (2004) 191.
16. C.S.C. Bose, S. Basak and K. Rajeshwar, *J. Electrochem. Soc.* **139** (1992) L75.
17. W.S. Huang, B.D. Humphrey and A.G. MacDiarmid, *J. Chem. Soc., Faraday Trans. I* **82** (1986) 2385.
18. J.R. Rodrígues, S. Gutiérrez, J.G. Ibañez, J.L. Bravo and N. Batina, *Environ. Sci. Tech.* **34** (2000) 2018.
19. C.Q. Cui, X.H. Su and J.Y Lee, *Pol. Degr. Sta.* **41** (1993) 69.
20. A.Q. Zhang, C.Q. Cui and J.Y. Lee, *Synth. Metals* **72** (1995) 217.
21. D. Stilwell and S-M Park, *J. Electrochem. Soc.* **136** (1989) 688.
22. P. Seymour, *J. Chem. Edu.* **76** (1999) 927.