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Reduction of hexavalent chromium using polyaniline films. Effect of film thickness, potential and flow velocity on the reaction rate and polymer stability

L.A.M. RUOTOLO* 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: pluis@iris.ufscar.br)*

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Abstract

Reduction of very toxic hexavalent chromium (Cr(VI)) to its trivalent state (Cr(III)) is necessary to facilitate the treatment of wastewater by precipitation or adsorption. The present study proposes the use of thin films of polyaniline on a conducting substrate for this purpose. The reduction rate of hexavalent chromium and the degree of degradation of the polyaniline film were studied as a function of the solution flow velocity, applied potential and film thickness. The reduction rate was significantly affected by the flow velocity, while the film thickness was observed to have little effect. The potential had no effect on the reduction rate within the range studied. The current efficiency was 100% in all experiments and no significant degradation of polyaniline was observed.

1. Introduction

Wastes containing hexavalent chromium are generated by a large variety of industries, such as metal finishing, dying, electronics, metallurgy and others. Due to the toxic effects of Cr(VI) (e.g. its cytotoxic, genotoxic and carcinogenic effects) the discharge of wastes, even with low concentrations of Cr(VI), is strictly controlled [1, 2].

The two most common oxidation states of chromium found in nature are +3 and +6. It is reported that compounds of Cr(III) are 10 to 100 times less toxic than those of +6 [3]. Also, while Cr(VI) is extremely mobile in nature, Cr(III) can be readily precipitated or adsorbed by a wide range of organic and inorganic substrates at neutral pH. In this light, the toxicity and mobility of Cr(VI) can be diminished by its reduction to Cr(III).

Nowadays the processes for Cr(VI) reduction use chemical reagents, such as sulfur dioxide or sodium metabisulfite. These reagents are consumed in the chemical reaction and cannot be recovered for reuse. The use of these reagents also increases the volume of sludge generated. After Cr(VI) reduction, the Cr(III) is precipitated in the form of hydroxides and the sludge generated is dried and stored.

The development of new technologies to improve or substitute the above conventional process is economically and environmentally desirable. Several alternatives have been studied, for example, adsorptive [4, 5], photochemical [6] and electrochemical processes [7, 8]. Among the electrochemical processes, the direct electroreduction of Cr(VI) was attempted using carbon substrates such as reticulated vitreous carbon (RVC) [9]. However, this process is economically unfavorable because of the low reaction rates and current efficiencies obtained. To solve this problem, a modification was proposed: indirect reduction employing a redox mediator such as $Fe^{2+/3+}$. This process is very efficient and with progress in membrane technology, offers promise of implementation [9].

Processes using conducting polymers deposited on substrates with large surface areas as mediator films, eliminates the necessity of a separation step in the $Fe^{2+/3+}$ process. Among the various applications of conducting polymers, their use in a chemical process for hexavalent chromium reduction has recently been discussed [3, 9]. This process is based on the spontaneous electron transfer from the polymer chain to the Cr(VI) present in dilute acid solutions.

The process employing conducting polymers starts with its deposition on an electrode substrate and then its immersion in a solution containing Cr(VI). The polymer is oxidized and the Cr(VI) is reduced to Cr(III). The polymer can be reduced again by applying a cathodic potential, and it can then be used in a new cycle [10–12]. However, the use of a conducting polymer as described above (under open circuit potential conditions) was not ideal because of over oxidation of the polymer and its consequent degradation, which can make the process inapplicable on an industrial scale. A spectrophotometric study by Malinauskas and Holze [13] using polyaniline for the reduction of Cr(VI) showed that the contact of the polyaniline film with the 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. The main product of degradation of polyaniline is *p*-benzoquinone [14, 15]. Before the degradation problem the continuous application of a negative potential to the film in order to maintain polymer stability was tested. The results of this procedure were positive, since film degradation was eliminated [16] and the conducting polymer acted as an electrocatalyst, increasing the reaction rate of reduction of Cr(VI) [17].

In order to effectively apply this modified process (which we call a cathodic protection process) in an industrial application, it was necessary to clarify the effect of the film thickness, potential and flow velocity on the reaction rate and stability of the film. Polyaniline was chosen because it is stable and easily synthesized in aqueous solution, and also because the monomer is very cheap.

2. Experimental

The electrochemical flow cell used is shown schematically in Figure 1. All potentials are referred to the Ag/AgCl system in 3.0 M KCl, (207 mV vs standard hydrogen electrode (SHE)). The cathode active area was 2.5 cm^2 and the cross sectional area for electrolyte flow was 0.5 cm^2.

The cathode was coated with a thin film of potentiodynamically deposited polyaniline. The potential range was −0.1 to +0.8 V vs Ag/AgCl and the sweep rate was 50 mV s^{-1}. The number of deposition cycles was varied according to the film thickness desired. The electrolyte was composed of 1.0 M H_2SO_4 plus 0.1 M aniline monomer (Mallinckrodt). The monomer was previously distilled under vacuum using zinc powder.

An Autolab PGSTAT30 potentiostat (Eco Chemie) was used for potential control.

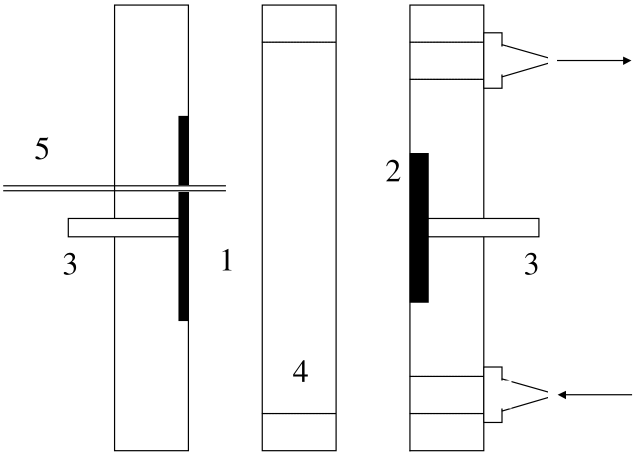

Fig. 1. Schematic representation of the electrochemical cell: (1) anode (Ti–RuO_2 DSA®); (2) cathode (vitreous carbon plate); (3) electric contacts; (4) electrolyte flow space; (5) Luggin capillary.

After electrosynthesis, the polyaniline film was washed with 1.0 M H_2SO_4 in order to eliminate monomer and oligomer residues. The electrochemical response of the film was then recorded at 50 mV s^{-1} in 1.0 M H_2SO_4 in the absence of the monomer.

When the polyaniline film had been synthesized, the electroreduction of Cr(VI) was initiated. 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. For each experiment a volume of 150 cm^3 1.0 M H_2SO_4 conatining 50 mg dm^{-3} Cr(VI) was used. The Cr(VI) source was potassium dichromate (Merck).

In order to avoid polymer degradation under open circuit potential conditions, the potential was applied before contact with the Cr(VI) solution was permitted. Only after the potential had been applied, was the peristaltic pump (with the flow velocity previously adjusted) turned on. At this point the reaction started and the chromium concentration and the electric current were measured using the UV–Vis spectrophotometer and the potentiostat, respectively.

At the end of each experiment the electrolyte was removed from the cell and the electrochemical response of the film was recorded in 1.0 M H_2SO_4 as described previously. The comparison of the voltammograms before and after the reaction with Cr(VI) permitted an evaluation of the polymer stability.

When all the stages of each experiment were completed, the polymer was stripped off the electrode surface using a solution of H_2O_2/H_2SO_4 (1:10 v/v) and then the electrode was polished with sandpaper and alumina (0.1 μm) to prepare it for a new experiment.

Twenty seven experiments were run following a factorial experimental design of three levels and three factors (3^3) [18]. The three factors studied were solution flow velocity, potential and film thickness. The three levels of flow velocity were established using a peristaltic pump. The three levels of film thickness were established indirectly, based on the work of Stilwell and Park [19], in which the film thickness is shown to be directly proportional to the height of the first anodic current peak in the voltammograms, i_p. Thus, when the first anodic current peak in the voltammogram of polyaniline electrosynthesis reached a desired value, the process of synthesis was stopped. The levels of the factors used, as well as the experimental design code, are shown in Table 1.

The reagents used in all experiments were of analytical grade and deionized water was used to prepare all the

Table 1. Actual and coded levels of the factors studied

Code	$v \times 10^3$ /m s^{-1}	i_p /mA cm^{-2}	E vs Ag/AgCl /V
−1	0.7	0.58	−0.1
0	2.0	1.06	+0.2
+1	3.3	1.54	+0.5

solutions. The temperature of the electrolyte was maintained in the range 25–28 °C.

3. Results and discussion

Figure 2 shows a typical series of voltammograms obtained during polymer electrosynthesis. From the electrochemical responses, the ratio of the heights of anodic current peaks before (i_{pb}) and after (i_{pa}) reaction with Cr(VI) (i_{pa}/i_{pb}) was calculated. This ratio was used as a measure of the polyaniline film stability. As an illustration, typical electrochemical responses before and after Cr(VI) reduction are shown in Figure 3. The voltammograms in Figure 3 correspond to the lowest value of the ratio i_{pa}/i_{pb} observed (i.e. the greatest extent of film degradation). The values of the ratio i_{pa}/i_{pb} for the other experiments can be seen in Appendix 1.

A typical normalized concentration profile (C/C_0) for the reduction of Cr(VI) is shown in Figure 4. From the variation of concentration with time it is possible to calculate the reaction rate, R, in mg m^{-2} s^{-1}. The values of R for the 27 experiments are shown in Appendix 1.

Some response surfaces for the reaction rate as a function of the coded flow velocity (v'), film thickness (i'_p) and potential (E') are shown in Figures 5–7 (where v', i'_p and E' are dimensionless). The other response surfaces have a similar morphology and are therefore not shown.

Considering only the significant effects, the following equation corresponds to the surface responses shown in Figures 5–7:

$$R\ (\mathrm{mg\,m^{-2}\,s^{-1}}) = 1.154 + 0.835v' - 0.151v'^2 \qquad (1)$$

The degree of significance adopted for the least-squares fitting was 95%, which gives a good correlation coefficient (R^2) of 0.97783. The residue distribution did not

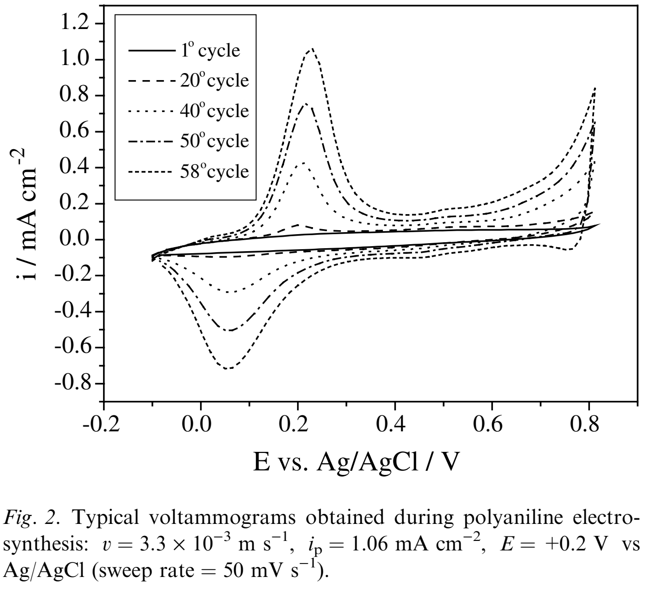

Fig. 2. Typical voltammograms obtained during polyaniline electrosynthesis: $v = 3.3 \times 10^{-3}$ m s^{-1}, $i_p = 1.06$ mA cm^{-2}, $E = +0.2$ V vs Ag/AgCl (sweep rate = 50 mV s^{-1}).

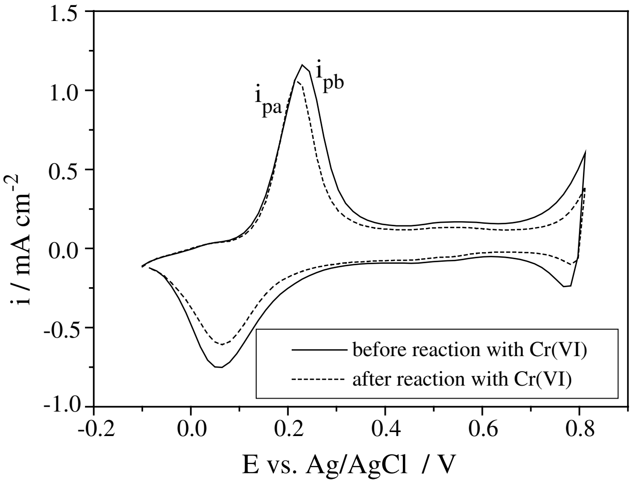

Fig. 3. Typical electrochemical response for polyaniline in 1.0 M H_2SO_4: $v = 3.3 \times 10^{-3}$ m s^{-1}, $i_p = 1.06$ mA cm^{-2}, $E = +0.2$ V vs Ag/AgCl (sweep rate = 50 mV s^{-1}).

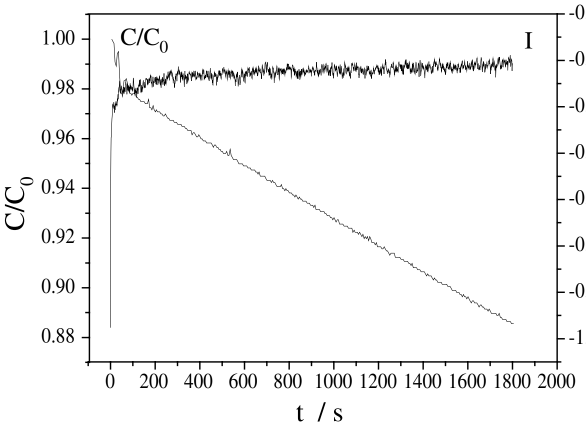

Fig. 4. Current and normalized concentration depletion as functions of the process time: $v = 3.3 \times 10^{-3}$ m s^{-1}, $i_p = 1.06$ mA cm^{-2}, $E = +0.2$ V vs Ag/AgCl.

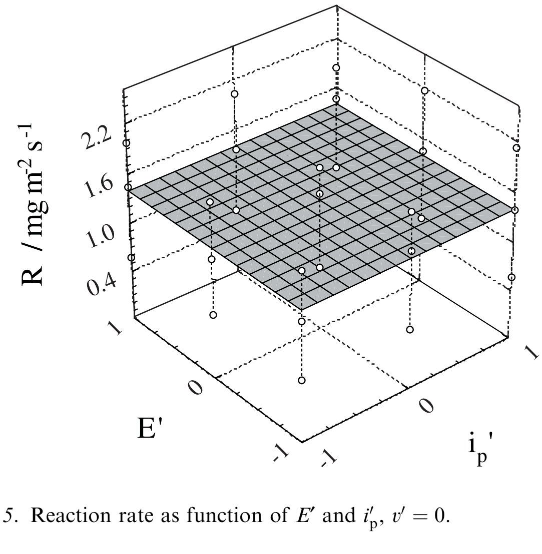

Fig. 5. Reaction rate as function of E' and i'_p, $v' = 0$.

follow a pattern, meaning that the fitting is adequate and no variable transformation is necessary.

Analyzing Equation 1 the potential and film thickness, within the range of concentration studied has no effect on the reaction rate (see also Figure 6). On the other hand, observing the graphs in Figures 7 and 8, a significant influence of flow velocity on the reaction rate can be seen. The square of the flow velocity had little effect on the reaction rate as can be verified from the small curvature in Figures 6 and 7 and the low value of the fitting coefficient of v'^2. No interaction effects between the variables were observed.

The absence of any effect of potential in this large range, as we can see from Figures 5–7 and in Equation 1, indicates that mass-transfer is the rate-determining step. As mass transfer controls the kinetics, all Cr(VI) is reduced when it reaches the outside of the polymer layer, which explains the fact that film thickness has no influence on the reaction rate. The kinetic potential independence is particularly interesting when working with polyaniline deposited on porous electrodes (such as RVC) where there is an internal potential profile along the path of the electric field, creating 'dead' zones where many reactions do not take place. In the present case, as the spontaneous reaction of Cr(VI) does not depend on potential over a large range, it would be possible to use a fully active porous electrode.

By integrating the current versus time curves, the charge passed can be determined, and the current efficiency calculated using the ratio of the charge used for the Cr(VI) reaction and the total charge passed. Current efficiency was 100% in all experiments, i.e., the charge supplied was exclusively used for the reduction of Cr(VI) to Cr(III). As no parallel reactions occur and the process is mass transfer controlled, it can be supposed that the reaction occurs under limiting current control.

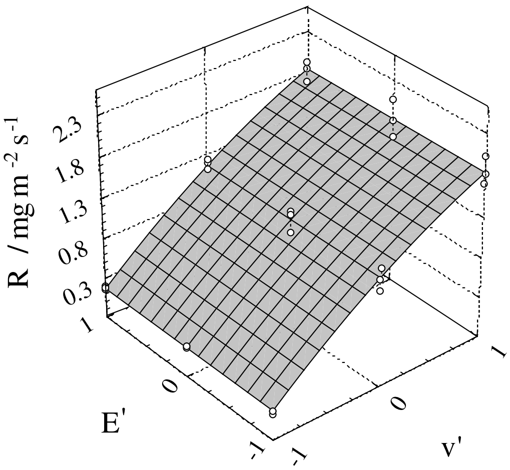

Fig. 6. Reaction rate as function of E' and v', $i'_p = 0$.

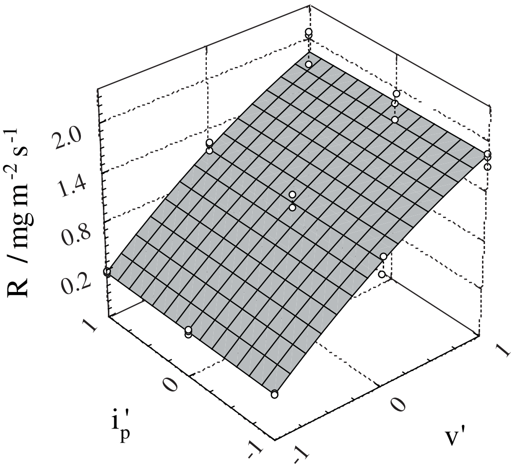

Fig. 7. Reaction rate as function of v' and i'_p, $E' = 0$.

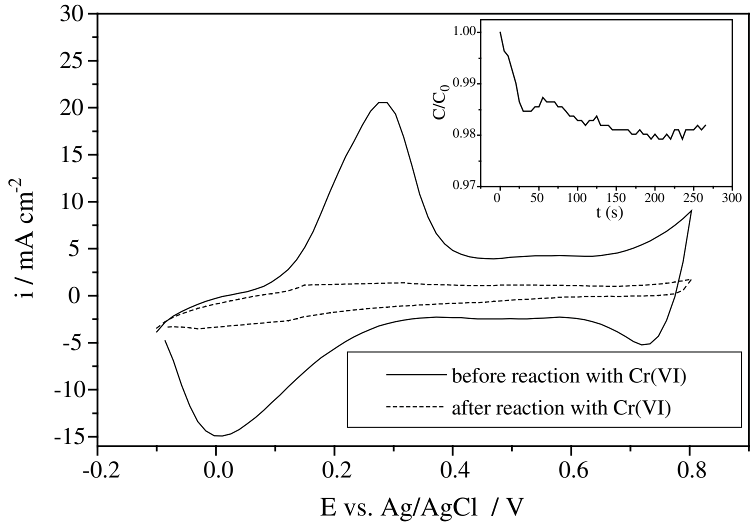

Fig. 8. Electrochemical response the polyaniline films before and after reaction with Cr(VI) when the process was carried out under open circuit conditions. Inset: Cr(VI) depletion as function of time: $v = 2.0 \times 10^{-3}$ m s^{-1}, $i_p = 1.05$ mA cm^{-2} (sweep rate = 50 mV s^{-1}).

For this reason the mass transfer coefficients can be calculated according to Equation 2:

$$k_m = \frac{I_{\text{lim}}}{zFAC} \tag{2}$$

where A is the electrode area, C the molar bulk concentration of Cr(VI) and I_{lim} the limiting current. The values of I_{lim} for each experiment were taken directly from Figure 4.

The values of k_m were 2.5×10^{-6}, 4.4×10^{-6} and 6.6×10^{-6} m s^{-1} for velocities of 0.7×10^{-3}, 2.0×10^{-3} and 3.3×10^{-3} m s^{-1}, respectively, which means that the process is under a laminar flow. Doubling the velocity also doubles k_m and the values are in agreement with literature [20].

Since there were no significant losses in the electrochemical activity of polyaniline films after reaction with Cr(VI) (Figure 3), the ratio between the anodic current density peaks taken before and after each reaction (i_{pa}/i_{pb}) is 1.00 in most of the experiments (see table in Appendix 1). As no changes in the electrochemical activity were observed, it can be concluded that cathodic protection conditions were very effective in preventing polymer degradation during Cr(VI) reduction. The values of i_{pa}/i_{pb} are shown in Appendix 1; they are not treated statistically because they presented no tendencies. The three variables studied had no influence on polymer stability under cathodic protection conditions.

Figure 8 shows voltammograms recorded before and after reaction with Cr(VI) for the process carried out under open circuit conditions. The voltammogram recorded after the reaction is practically the same as that of uncovered vitreous carbon, suggesting that the polymer was entirely consumed in a chemical degradation reaction [14]. Thus, open circuit conditions are not suitable for practical application because of polymer degradation. As well as polymer degradation it can be observed in Figure 8 (see inset) that Cr(VI) depletion was not significant when compared with the process carried out under cathodic protection conditions.

4. Conclusions

The potential independence of the reaction rate within the range of flow velocities studied suggests that mass transfer is the rate-limiting step in the process of Cr(VI) reduction using polyaniline. As the reaction is controlled by mass-transfer, the reduction of Cr(VI) occurs on the outside of the polymer layer, so the film thickness has no effect on this process. A further step would be to study the effect of applied potential on the reaction rate of Cr(VI) reduction using a wide range of concentrations and flow velocities.

The cathodic protection of the polyaniline film proved to be very effective in preserving the polymer stability.

Acknowledgement

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References

1. D.E. Kimbrough, Y. Cohen, A.M. Winer, L. Creelman and C. Mabuni, *Critical Rev. Environ. Sci. Tech.* **29** (1999) 1.
2. H.G. Seiler, H. Sigel and A. Sigel, 'Handbook on Toxicity of Inorganic Compounds' (Marcel Dekker Inc., New York, 1988).
3. C. Wei, S. German, S. Basak and K. Rajeshwar, *J. Electrochem. Soc.* **140** (1993), L60.
4. M.P. Candela, J.M.M. Martinez and R.T. Maciá, *Wat. Res.* **29** (1995) 2174.
5. D. Petruzzelli, R. Passino and G. Tiravanti, *Ind. Eng. Chem. Res.* **34** (1995) 2612.
6. W.Y. Lin, C. Wei and K. Rajeshwar, *J. Electrochem. Soc.* **140** (1993) 2477.
7. S. Goeringer, N.R. Tacconi, C.R. Chenthamarakshan and K. Rajeshwar, *J. Appl. Electrochem.* **30** (2000) 891.
8. K.N. Njau and L.J.J Janssen, *J. Appl. Electrochem.* **29** (1999) 411.
9. R. Senthurchelvan, Y. Wang, S. Basak and K. Rajeshwar, *J. Electrochem. Soc.* **143** (1996) 44.
10. M.A. Alatorre, S. Gutiérrez, U. Páramo and J.G. Ibañez, *J. Appl. Electrochem.* **28** (1998) 551.
11. J.R. Rodrígues, S. Gutiérrez, J.G. Ibañez, J.L. Bravo and N. Batina, *Environ. Sci. Tech.* **34** (2000) 2018.
12. W.A. Wampler, S. Basak and K. Rajeshwar, *Carbon* **34** (1996) 747.
13. A. Malinauskas and R. Holze, *Ber. Bunsenges. Phys. Chem.* **102** (1998) 982.
14. C.Q. Cui, X.H. Su and J.Y. Lee, *Polymer Degrad and Stability* **41** (1993) 69.
15. A.Q. Zhang, C.Q. Cui and J.Y. Lee, *Synth. Metals* **72** (1995) 217.
16. L.A.M. Ruotolo and J.C. Gubulin, Proceeding of 2001 Joint Meeting of ECS and ISE (San Francisco, USA, 2001), p. 481.
17. Y. Wang and K. Rajeshwar, *J. Electroanal. Chem.* **425** (1997) 183.
18. D.C. Montgomery, 'Design and Analysis of Experiments' (John Wiley & Sons, New York, 1991), p. 649.
19. D.E. Stilwell and S.M. Park, *J. Electrochem. Soc.* **135** (1988) 2491.
20. L. Lipp and D. Pletcher, *Electrochim. Acta* **42** (1997) 1101.

Appendix 1

Reaction rates of the Cr(VI) reduction and stability of the polymer films.

v'	i'_p	E'	i_{pa}/i_{pb}	R /mg m^{-2} s^{-1}
−1	−1	−1	1.00	0.16
−1	−1	0	0.95	0.18
−1	−1	+1	0.96	0.16
−1	0	−1	1.00	0.12
−1	0	0	1.00	0.17
−1	0	+1	1.00	0.19
−1	+1	−1	0.97	0.16
−1	+1	0	1.00	0.19
−1	+1	+1	0.96	0.18
0	−1	−1	0.95	1.00
0	−1	0	1.00	0.99
0	−1	+1	1.00	1.20
0	0	−1	1.00	1.26
0	0	0	1.00	1.26
0	0	+1	1.00	1.10
0	+1	−1	1.00	1.14
0	+1	0	1.00	1.21
0	+1	+1	1.00	1.23
+1	−1	−1	1.00	1.70
+1	−1	0	1.00	1.82
+1	−1	+1	1.00	1.85
+1	0	−1	1.00	1.82
+1	0	0	0.92	1.62
+1	0	+1	1.00	1.93
+1	+1	−1	0.93	2.04
+1	+1	0	0.94	2.08
+1	+1	+1	1.00	1.69