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DEGRADATION OF POLYPYRROLE-MODIFIED ELECTRODES IN A CHLORIDE CONTAINING MEDIUM

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Abstract: The behaviour of a polypyrrole-modified electrode in an aqueous 0.5 M HCl solution at high anodic potentials was studied. Electrochemical experiments and ^{13}C -NMR analysis showed a decrease in conductivity, due to the formation of C-Cl bonds in the pyrrole ring structure.

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Since the extensive use of polypyrrole for polymer-modified electrodes¹⁻⁴, several authors^{5,6} have found that anodic polarization of a polypyrrole electrode in a halogen ion containing solution causes a decrease in conductivity of the polymer. Especially, oxidation of chloride ions at potentials higher than + 1.0 V vs. SCE causes a dramatic effect⁶. We studied this effect in an aqueous solution of hydrochloric acid by electrochemical techniques and by ^{13}C -NMR measurements.

Experimental

The polypyrrole films were formed on a platinum disc of ca. 0.5 cm² from an aqueous solution of 0.1 M LiClO₄ with 1 vol.-% (ca. 0.14 M) pyrrole. The films were deposited either under potentiostatic conditions ($E = + 600$ mV vs. SCE) or under galvanostatic conditions ($i = 2$ mA/cm²). The film thickness was controlled by measuring the charge, used to form the film (since $\rho = 1.48$ g/cm³, 100 mC/cm² charge corresponds to 0.28 μm thickness^{2,4}).

The voltammetric experiments for an electrode covered with a polypyrrole film in an aqueous 0.5 M HCl solution at 25°C were carried out in a three-compartment cell. A saturated calomel electrode (SCE) was used as the reference electrode. The voltammograms were recorded at a scan rate of 10 mV/s.

Results

Figure 1 shows characteristic i - E curves for a polypyrrole electrode in 0.5 M HCl. During the

first anodic sweep, indicated by 1 in the figure, a peak is detected at 950 mV vs. SCE. It has been found that this is caused by oxidation of the polypyrrole backbone. The peak at 1200 mV during the first anodic sweep is caused by oxidation of chloride ions, because in a similar experiment with 0.5 M H₂SO₄ as electrolyte this peak was not present. No reduction current is observed during the cathodic sweep. During the second anodic sweep, also starting at 900 mV, the current was much smaller than during the first anodic sweep, and at potentials higher than 1600 mV oxidation of water to oxygen occurs at the polypyrrole/platinum interface resulting in oxygen bubble formation and peeling of the polymer film from the platinum substrate. The chloride concentration remains practically constant during the sweep experiments. The decrease in the height of the peak at 1200 mV may be caused by either increase of electrode resistance or decrease in number of active sites for the oxidation of chloride ions or by both.

The effect of the anodic polarization of a polypyrrole electrode in a chloride containing medium on its conductivity was studied. The potential difference between the working electrode and the counter electrode in a one-compartment electrolysis cell was measured as a function of the time of polypyrrole film formation. The film was formed galvanostatically at a current density of 2 mA/cm² on a Pt-substrate and on polypyrrole films which were already present on a Pt substrate.

Curve A_1 of figure 2 shows the potential difference vs. time curve during the formation of the first layer of polypyrrole on a Pt-substrate. After a 5 min. polarization the polypyrrole electrode was removed from the ClO_4^- -pyrrole formation solution, rinsed and dried. Then a second layer of polypyrrole was formed on the electrode; the ΔE vs. t curve is given by B_1 of figure 2: the potential difference has been increased by ca. 13%.

Curve B_2 of figure 2 shows the result of an experiment when, between the formation of the first (curve A_2) and second layer of polypyrrole, the electrode was polarized in 0.5 M HCl from 900 to 1500 mV vs. SCE at a scan rate of 10 mV/s. The increase in E vs. time may be caused by formation of atomic chlorine which reacts with the newly formed polypyrrole. During the formation of the second layer chloride ions are present in the pores of the first polypyrrole layer. It can be concluded that by the anodic polarization in 0.5 M HCl the potential difference has been increased by more than 30%. From this result and the voltammetric behaviour of a polypyrrole electrode in 0.5 M HCl (Fig. 1) it follows that the decrease in conductivity may be caused by distortion of the π -system of conjugated double bonds of the polymer, due to addition of chlorine to the carbon backbone. The "chlorinated" polymer was investigated by ^{13}C -NMR technique (using magic angle spinning). The spectrum of figure 3 was obtained using a delrin spinner. The spectral range between 100 and 80 ppm from TMS was obscured. The spectrum between 110 and 140 ppm may be contributed to the polypyrrole backbone⁷. The peaks at 69 and 30 ppm probably indicate covalent C-Cl bonds in the chlorinated polypyrrole.

Fig. 1. i - E curve of a 1.68 μm thick polypyrrole film on Pt in 0.5 M HCl/ H_2O .

Conclusion

Anodic polarization of polypyrrole films in a solution with chloride ions leads to a degradation of the polymer due to the addition of chlorine to the pyrrole ring structure. The chlorine atoms are covalently bound to the carbon atoms.

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Fig. 2. ΔE vs. t curves for polypyrrole formation on a platinum disc (A), on an already formed polypyrrole layer (B), with (subscript 2) and without (subscript 1) "chlorination".

Fig. 3. ^{13}C -NMR spectrum of polypyrrole, after "chlorination" in 0.5 M HCl.