

Electrogeneration of polythiophene films: temperature influence and electrical properties

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(Received 15 September 1988; revised 29 May 1989; accepted 7 June 1989)

Polythiophene films were electrogenerated between -12 and 60°C by polarization at 1700 mV . The polymer films were studied at ambient temperature in the background electrolyte by cyclic voltammetry and potential steps techniques. From the polymer weight, the polymerization current efficiency and the charge storage efficiency were obtained. Both parameters increased in the temperature range studied, when the temperature decreased. The charge storage is related to a very strong nucleation process attributed to the formation of a polymer-perchlorate compound.

(Keywords: polythiophene; electrogeneration; charge storage; current efficiency)

INTRODUCTION

Chemical and electrochemical parameters have a great influence on the electrogeneration of conducting polymer films and on their physical properties¹⁻⁶. The most important technological physical properties are related to the oxidation/reduction polymer ability. This process needs counterion diffusion from electrolyte (the film has electronic and ionic conductivity) to retain electro-neutrality. Counterion inclusion promotes a conductivity change of several orders of magnitude⁷⁻¹⁰. The most efficient way to oxidize and reduce polymer films reversibly is by electrochemical methods¹¹⁻¹⁵.

The marked influence of temperature on the electro-generation of polythiophene films was pointed out previously¹. The polymer films were generated there by cyclic voltammetry. In the work reported here our aim was to investigate polymer layer electrogeneration using a constant potential polymerization at different temperatures. The polymer films produced were studied by means of different electrochemical methods to obtain information about the influence of temperature on charge storage capacity, polymer conductivity, polymer production, etc.

EXPERIMENTAL

The monomer (Merck A.G.) was washed (three times) with a 10% NaOH aqueous solution. Then it was washed using ultra-pure water (from a Mill Pore Milli Q. Reagent Water System) to eliminate NaOH. The monomer was then distilled twice under vacuum and used to prepare the working solutions.

LiClO_4 (Jansen A.G.) was used as electrolyte. This salt was dehydrated at 80°C for 24 h before use.

Acetonitrile was used as solvent. It was distilled twice, in the presence of P_2O_5 , to eliminate water. A water content (obtained by Karl-Fischer analysis) of $<0.04\%$ was attained.

All the solutions were deaerated by bubbling N_2 at ambient temperature for 10 min and thermostated under

an inert atmosphere by passing N_2 over the solution before the current flow.

The polymer film was electrogenerated using potential steps from -500 to 1700 mV generated by a Wenking DPC 72 generator joined to a Wenking ST 72 potentiostat. The current flow time response was stored in an IBM PC AT computer and plotted using a 7475A HP plotter.

The electrochemical behaviour of the polymer films was checked by means of a triangular potential sweep and a potential step in 0.1 M LiClO_4 solution. Potential sweeps were generated as above, using a Wenking VSG 72 generator.

A 0.5 cm^2 platinum sheet was used as the working electrode. A platinum sheet, several square centimetres in surface area, was used as the counter electrode. A saturated Calomel electrode was used as reference electrode. All potentials in this work are related to it. A one-compartment electrochemical cell was used. The working electrode and the reference electrode were connected by means of a salt bridge containing the background solution.

The cell was immersed in a thermostated bath ($\pm 0.5^{\circ}\text{C}$). The amount of polymer formed on the electrode was determined gravimetrically using an ultra-micro Sartorius (10^{-7} g) balance.

RESULTS AND DISCUSSION

The variation in current densities (I) obtained with the working electrode subjected to a polarization at 1700 mV over 120 s (in 0.1 M LiClO_4 and 0.25 M thiophene acetonitrile solution) at different temperatures is shown in *Figure 1*. At 60°C a continuous decrease of the current density is observed after the initial sharp current density maximum (related to the charge of the double layer). At lower temperatures a nucleation process is observed on the I vs. t plot: a minimum of current density appears after the short initial maximum. This minimum is related to polymer nucleation and growth on the electrode. On the I vs. t plot obtained at 40°C a second maximum of

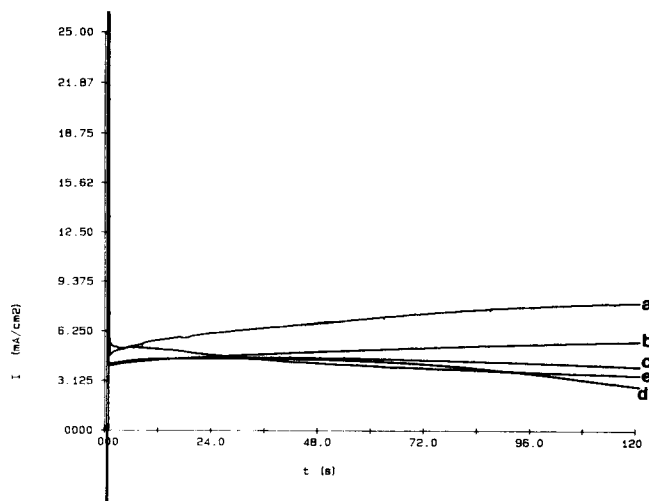


Figure 1 Plots of I vs. t obtained in 0.1 M LiClO_4 plus 0.25 M thiophene in acetonitrile at different temperatures ($^{\circ}\text{C}$): (a) -12 ; (b) 0 ; (c) 20 ; (d) 40 ; (e) 60 . The plots were generated by a potential step from -500 mV to $+1.700$ mV

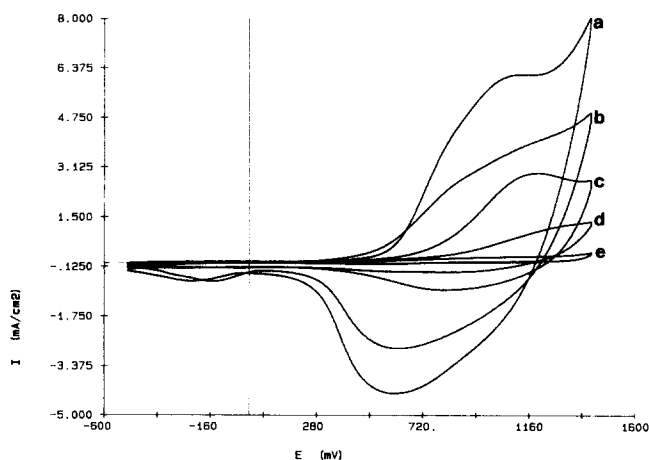


Figure 2 Cyclic voltammograms obtained by cyclic voltammetry at 50 mV s^{-1} in 0.1 M LiClO_4 in acetonitrile solution at ambient temperature using polythiophene films generated under the experimental conditions of *Figure 1*

current density is observed after 25–30 s. This can be related to a loss of conductivity of the generated polymer layer. At lower temperatures this maximum does not appear in the time range under study.

The loss in conductivity at higher polymerization temperatures can also be deduced from the control voltammograms (*Figure 2*) obtained from the electro-generated film in the background solution at ambient temperature and under inert atmosphere. A decreasing slope is observed ($I/E = 1/R$) on the anodic branches at increasing temperatures and for anodic over potentials greater than 500 mV which indicates that resistance increases with polymerization temperature.

Both electrochemical processes (polymer oxidation and reduction) observed in *Figure 2* are related to the nucleation of new phases, i.e. of a polythiophene-perchlorate ion complex with anodic potentials and the undoped polythiophene with cathodic potentials. The plot of I vs. t obtained from the background solution at ambient temperature when the polymer films, at different temperatures, were subjected to a potential step from -400 mV (in the potential range related to the reduced state, *Figure 2*) to 1000 mV are shown in *Figure 3*. A

nucleation process is observed 0.2 s after the potential step. The area under the plot of I vs. t is related to the ability of the polymer layer to store charge. The time needed to oxidize the polymer layer is > 10 s, as can be deduced from the figure. The more conducting films show a well defined maximum of current density after the minimum of nucleation.

Reduction processes are faster than the above oxidation processes. *Figure 4* shows the plot of I vs. t obtained from the inverse potential step (1000 mV to -400 mV). The nucleation process of the doped polythiophene phase is deduced from the change in slope. All the reduction processes were finished after 2 s. The presence of these nucleation processes has a great influence on physical properties if fast responses are required, such as electrochromic response. In this case, the nucleation process into the film can be responsible for the long time needed for the change of colour.

We tried to quantify the current efficiency of the electropolymerization process and the ability of the films formed at different temperatures to store electrical charge. The polymer films were weighed using an ultra-micro balance (10^{-7} g). We present the experimental results in *Table 1*. Polymer production increases as the temperature of the monomer solution decreases. The electrical charge spent on polymer formation, obtained by integration of

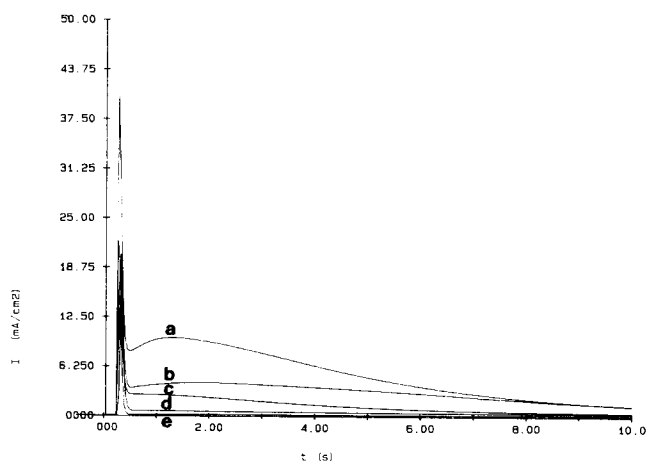


Figure 3 Plots of I vs. t obtained when polythiophene films obtained at different temperatures (see *Figure 1*) were subjected to a potential step from -400 mV to $+1.000$ mV in 0.1 M LiClO_4 in acetonitrile solution at ambient temperature

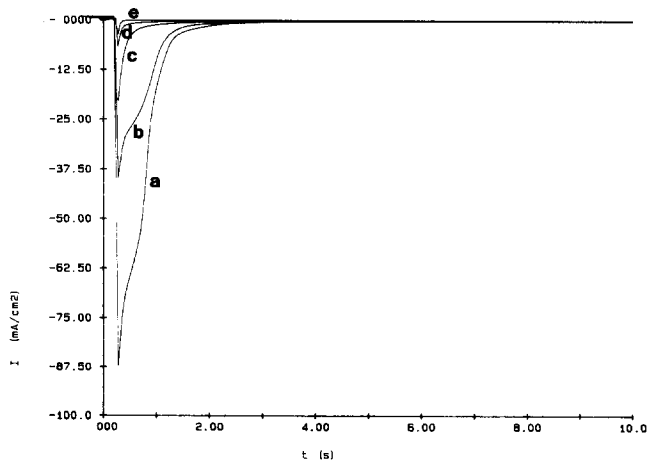
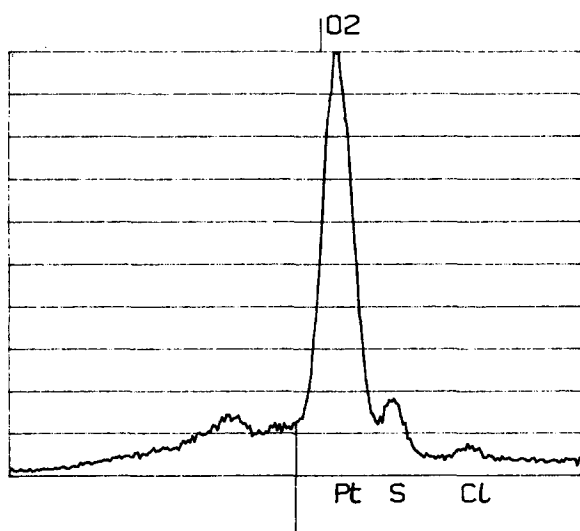


Figure 4 As for *Figure 3*, but with a cathodic step of potential from $+1.000$ mV to -400 mV

Table 1 Polymer production by polarization (on 1 cm² contact area of platinum) at 1700 mV for 120 s in 0.1 M LiClO₄ plus 0.25 M thiophene acetonitrile solution at different temperatures

T (°C)	Polymer (mg cm ⁻²)	Charge ^a (mC cm ⁻²)	10 ⁴ × Current efficiency ^b (mg mC ⁻¹)	Charge stored ^c (mC cm ⁻²)		Storage efficiency ^d (mC mg ⁻¹)	
				Q _{ox}	Q' _{ox}	Q _{ox}	Q' _{ox}
-12	0.3335	836.03	4	99.91	52.69	300	100
0	0.2335	610.59	3.8	63.53	30.26	272	129
20	0.1605	533.09	3.2	35.59	14.45	221	90
40	0.1406	491.92	2.9	14.24	5.30	101	37
60	0.1387	505.55	2.7	4.81	2.74	35	20

^a Electrical charge spent during polymerization^b Polymer weight ratio charge^c Electrical charge stored in the polymer immersed in background electrolyte when subjected to an anodic potential sweep (Q_{ox}) or an anodic potential step (Q'_{ox}) at ambient temperature^d Charge storage/polymer weight ratio**Figure 5** EDAX analysis of the coated electrode generated at 20°C

the area under the plot of I vs. t (Figure 1), increases as temperature decreases. The ratio of polymer weight and electrical charge gives the current efficiency and this increases as temperature decreases.

Another important parameter of these polymer films is their ability to store electrical charge, as mentioned above. The electrical charges related to polymer oxidation by means of a potential sweep (obtained by integration of the area under the anodic branch of Figure 2) or by a potential step (from Figure 3) are also listed in Table 1. The ratio between stored charge and polymer weight gives the charge storage efficiency at ambient temperature (control voltammograms and plots of I vs. t were obtained at ambient temperature in the background electrolyte). Charge storage efficiency at ambient temperature increases with decreasing polymerization temperature.

Figure 5 shows an EDAX from the coated electrode obtained at 20°C. The maximum related to X-ray emission from S to Cl atoms is not masked by the maximum related to the emission of the platinum electrode. Polymer growth and doping level were investigated by EDAX analysis.

CONCLUSIONS

A large increase in current efficiency (mg of polymer/mC) was observed when the temperature of polymerization decreased from 60 to -12°C. This suggests the presence of parallel reactions at high temperatures, giving non-polymeric products.

The polymer films formed at lower temperatures show greater charge storage efficiency (mC stored/mg of polymer). This seems related to greater conductivity of the films formed at lower temperatures.

The oxidation/reduction of the polymer films in the background solution is related to a nucleation process into the layer. Oxidation and reduction are probably responsible for the low transition times in processes like electrochromism where short response times are needed.

ACKNOWLEDGEMENTS

This work was supported by Basque Country University, Project UPV 20-3.215-24/87.

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