

# Charge–discharge characteristics of polythiophene as a cathode active material in a rechargeable battery

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Polythiophene films were electrochemically deposited on glassy carbon substrates under potentiostatic control and used as cathode active material together with a Zn anode in a rechargeable battery with propylene carbonate,  $\text{Zn}(\text{ClO}_4)_2$ ,  $\text{LiClO}_4$  electrolyte. Charge–discharge characteristics were studied. The average discharge voltage of the polythiophene/Zn cell was 1.25 V. In the low current density region (i.e.  $10\text{--}50 \mu\text{A cm}^{-2}$ ) the cycling coulombic efficiency was above 95%, but in the fast charge–discharge region, where current densities were  $0.1\text{--}0.5 \text{ mA cm}^{-2}$ , the coulombic efficiency decreased to 55% with increasing discharge rate. Additionally, it was found that the cyclic coulombic efficiency was a function of the charging depth.

Keywords: *Cathode materials, charge–discharge, glassy carbon substrates, polythiophene films*

## 1. Introduction

Polythiophenes can easily be prepared in the form of a thin film via electrooxidative polymerization of appropriate thiophene monomers (thiophene [1], bithiophene [2], 3-methylthiophene [5]) on certain substrates. In most previous studies polythiophenes were generated by galvanostatic [2] and potentiodynamic [5] methods. The peak potential of polythiophene oxidation lies in the range 0.8–1.4 V vs SCE [1, 4, 5, 6], depending on the type and the position of the substituent in the monomer unit.

There have been many studies of the electrochemical behaviour of polythiophenes [1, 3–5, 6], but relatively few data are available on the construction and performance of secondary batteries containing a polythiophene electrode [1, 4]. In the present study we have assembled and investigated a cell containing the electrochemically synthesized polythiophene (PT) as active cathode material and a Zn electrode as anode in a nonaqueous electrolyte.

## 2. Experimental details

The propylene carbonate (PC) was dried for two days by means of the anhydrous zeolite 4A. After drying, the residual water content was determined by gas chromatography to be 0.005%. Zinc perchlorate was dried in vacuum at 65 °C for 30 h. Lithium perchlorate was vacuum dried at 100 °C for 5 h, and was then melted and vacuum dried for 2 h in the molten state. All experiments were carried out at 25 °C in an argon atmosphere.

The electrolyte used in the PT/Zn battery contained 0.1 M  $\text{Zn}(\text{ClO}_4)_2$ , 1.0 M  $\text{LiClO}_4$  and PC. Its volume was roughly 5 cm<sup>3</sup>. Charging and discharging tests were conducted galvanostatically without signifi-

ficant rest between successive charge and discharge half cycles.

The polythiophene was prepared on a glassy carbon (GC) stick electrode (geometric working area of 0.064 cm<sup>2</sup>) in a three-electrode cell. Platinum foil and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. Thin film of polythiophene was synthesized potentiostatically at +1.6 V vs SCE for 60 s from a solution containing 1.0 M  $\text{LiClO}_4$  and 0.65 M thiophene in PC.

Cyclic voltammetry curves were obtained using a PAR (model 273) potentiostat/galvanostat.

## 3. Results and discussion

The polythiophene film, which was prepared in the manner described in the previous Section, was black in colour, compact and homogenous. During the synthesis of the polymer film the current increased approximately linearly with time. From this relationship we were able to calculate the total capacity,  $Q_s$ , of the formed film. For the previously described synthesis conditions total capacity was calculated to the amount 0.95 C cm<sup>-2</sup>. Preparation of films approximately 60 nm thick required about 24 mC cm<sup>-2</sup> [4]. Thus, the thickness of the PT film used for the experiments was about 2.5 μm.

### 3.1. Voltammetric analysis

For cyclovoltammetric investigation, after synthesis of the PT film, a PT/GC electrode was washed with pure PC and immersed in 1.0 M  $\text{LiClO}_4$ –PC solution. Typical cyclic voltammograms of a PT film on a GC surface are shown in Fig. 1.

The voltammograms show that the electrode can be repeatedly cycled with good reproducibility

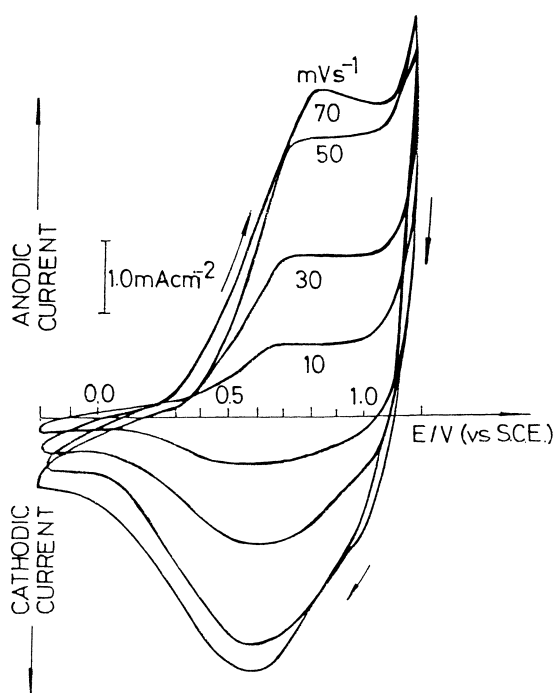


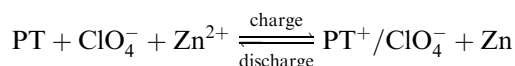
Fig. 1. Cyclic voltammograms of the PT/GC electrode (total film capacity  $Q_s = 0.95 \text{ C cm}^{-2}$ ) in the  $1.0 \text{ M LiClO}_4\text{-PC}$  solution at various scan rates at room temperature.

without any significant decomposition of the material. The anodic and the cathodic waves remain well defined. The coulombic efficiency, obtained by the expression  $Q_c/Q_a$ , is in the region of 80–99% ( $Q_c$  and  $Q_a$  are the integrated charges under the reduction and oxidation waves, respectively). These results point to a possible application of the PT/GC electrode in a rechargeable battery. The equilibrium potential of the PT/GC electrode in  $1.0 \text{ M LiClO}_4\text{-PC}$  is  $+0.65 \text{ V vs SCE}$  and the equilibrium potential of the  $\text{Zn/Zn}^{2+}$  electrode in the same electrolyte is  $-0.70 \text{ V vs SCE}$ .

Thus, there are appropriate conditions for formation of a Zn/polythiophene battery with a high voltage.

The Zn electrode used for this secondary cell has a geometric area of  $1.0 \text{ cm}^2$  which is much larger than the geometric area of the PT electrode. Thus, it worked as an unpolarized electrode, and its potential with respect to SCE was constant during the experiments. This fact was proven with a Zn/SCE couple. The change in cell voltage in this case can be attributed only to the changes in potential of the PT electrode alone.

The total process in the PT/Zn battery is represented by the reaction:



This equation involves oxidation of the polymer and compensation of the positive charge by the  $\text{ClO}_4^-$  ions, which diffuse from the electrolyte into the PT matrix (the process of p-doping during the charge of the battery) and reduction of the polymer with diffusion of the  $\text{ClO}_4^-$  ions from the matrix to the electrolyte (undoping process during the discharge of the battery).

### 3.2. Constant current charge–discharge characteristics

**3.2.1. Low current densities.** Typical charge–discharge curves of the PT-GC/Zn cell in the regime of low charge–discharge current densities ( $\sim 10 \mu\text{A cm}^{-2}$ ) are shown in Fig. 2. Charging was carried out at  $31 \mu\text{A cm}^{-2}$  and stopped when the voltage reached  $1.7\text{--}1.9 \text{ V}$ , because the cyclic voltammograms of the polythiophene electrode showed that above  $1.0 \text{ V vs SCE}$  secondary reactions were possible. Discharging was carried out to near zero cell voltage sequentially at the rates given in Table 1, with the cell always restored to the same initial charge after each

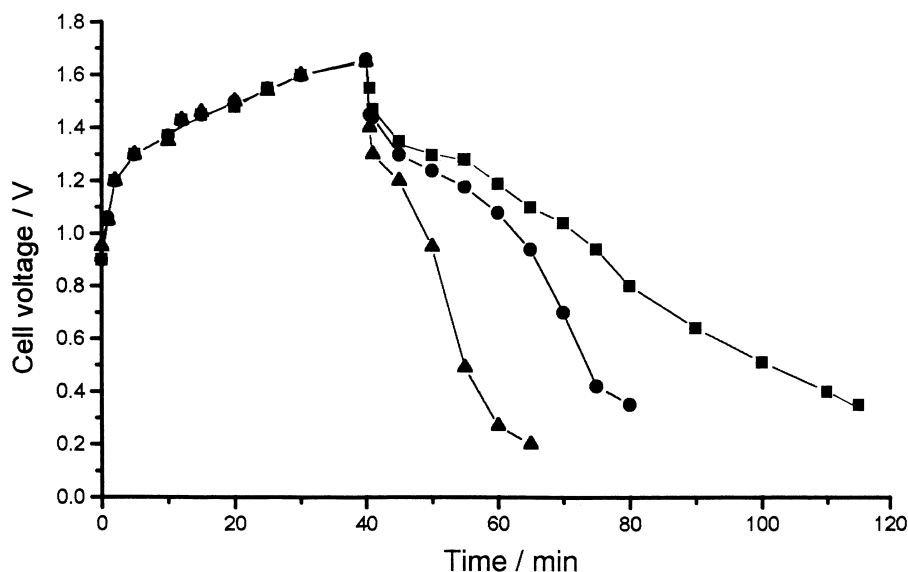


Fig. 2. Charging and discharging curves of the PT-GC/Zn cell at  $25^\circ\text{C}$ . Charging was carried out always at a current density of  $31 \mu\text{A cm}^{-2}$  up to charge density of  $74 \text{ mC cm}^{-2}$ . Discharge current density varied as follows: (■)  $15.5$ , (●)  $31.0$  and (▲)  $47.0 \mu\text{A cm}^{-2}$  (total film capacity  $Q_s = 0.95 \text{ C cm}^{-2}$ ).

Table 1. Coulombic efficiency and average discharge voltage at different constant discharge rates for the PT/Zn cell at room temperature

Discharge rate/ $\mu\text{A cm}^{-2}$	Average discharge voltage/V	Coulombic efficiency/%
15.5	1.30	96
31.0	1.25	99
47.0	1.25	98

Charging rate:  $31.0 \mu\text{A cm}^{-2}$ ; charging: up to  $74 \text{mC cm}^{-2}$ .

discharge. A flat region appears in all the discharge half-cycles. The cycling coulombic efficiency is high, above 95%, and it does not depend on the discharging rate (Table 1). The average discharge voltage of the cell is 1.25 V independently of the discharge current. The open circuit voltage of the charged and discharged cell is 1.65 V and 0.70 V, respectively.

The cyclic coulombic efficiency as a function of the charging depth of the polymer (i.e., charge loaded on polymer film in C divided by geometric area of the PT film) when charge and discharge rates were the same, that is  $31.0 \mu\text{A cm}^{-2}$ , is given in Table 2.

The coulombic efficiency decreases markedly with increasing charge depth. This decrease may be a consequence of the reduced exploitation of the active mass of the polythiophene in the depth of the film due to the slow diffusion of the ionic charge in the polymer structure during the discharge of the PT/Zn cell. Diffusion coefficients of the ions through polythiophene film are in the range  $10^{-9}$  to  $10^{-10} \text{cm}^2 \text{s}^{-1}$  [1], which is an indication of low ionic mobility. This behaviour is a disadvantage of the battery and investigations of the influence of the thickness and the structure of the polythiophene film on the cyclic efficiency at various charging depths are necessary.

### 3.3. High current densities

Typical charge-discharge curves of the PT/Zn battery in the region of high current densities ( $\sim 0.1 \text{mA cm}^{-2}$ ) are shown in Fig. 3. As in the low current region,

Table 2. Coulombic efficiency of the PT/Zn cell at different charging depths

Charge depth/ $\text{C cm}^{-2}$	Coulombic efficiency/%
0.074	99
0.11	72
0.20	64
0.40	56
0.48	52

Charging and discharging rates:  $31.0 \mu\text{A cm}^{-2}$ .

charging was always carried out at the current density of  $0.3 \text{mA cm}^{-2}$  until the voltage 1.70–1.95 V was reached. Discharging was carried out to near zero cell potential sequentially at the rates given in Table 3. The cell was always restored to the initial charge after each discharge. The optimum range of current densities for discharge is  $0.05$ – $0.2 \text{mA cm}^{-2}$ , when clear plateaus appear on the discharge half-cycles. When the discharge rate exceeded roughly  $0.2 \text{mA cm}^{-2}$ , the discharge curves did not show a flat region. As in the low discharging rate region the average discharge voltage was roughly 1.25 V.

The cyclic coulombic efficiency as a function of the discharging current density is shown in Table 3. In contrast to the low current density region in the high current density region the coulombic efficiency depends on the discharge rate. When the discharge current density increases from 0.1 to  $0.5 \text{mA cm}^{-2}$  the coulombic efficiency decreases from 98 to 60%.

Table 3. Coulombic efficiency at various discharging rates for the PT/Zn cell at room temperature

Discharge rate/ $\mu\text{A cm}^{-2}$	Average discharge voltage/V	Coulombic efficiency/%
100	1.25	98
160	1.25	97
310	1.25	80
480	1.20	60

Charging rate:  $0.3 \text{mA cm}^{-2}$ ; charging: up to  $47 \text{mC cm}^{-2}$ .

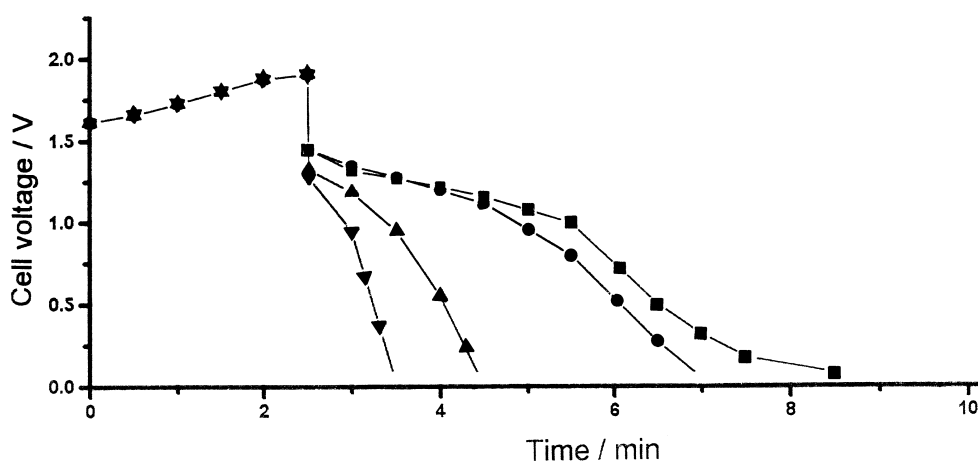


Fig. 3. Charge-discharge curves of the polythiophene on GC/LiClO<sub>4</sub>, Zn(ClO<sub>4</sub>)<sub>2</sub>, PC/Zn battery. Charging was done at a current density of  $0.3 \text{mA cm}^{-2}$  up to charge density of  $47 \text{mC cm}^{-2}$ . Discharging current density varied as follows: (■) 0.1, (●) 0.16, (▲) 0.31, (▼)  $0.48 \text{mA cm}^{-2}$  (total film capacity  $Q_s = 0.95 \text{C cm}^{-2}$ ).

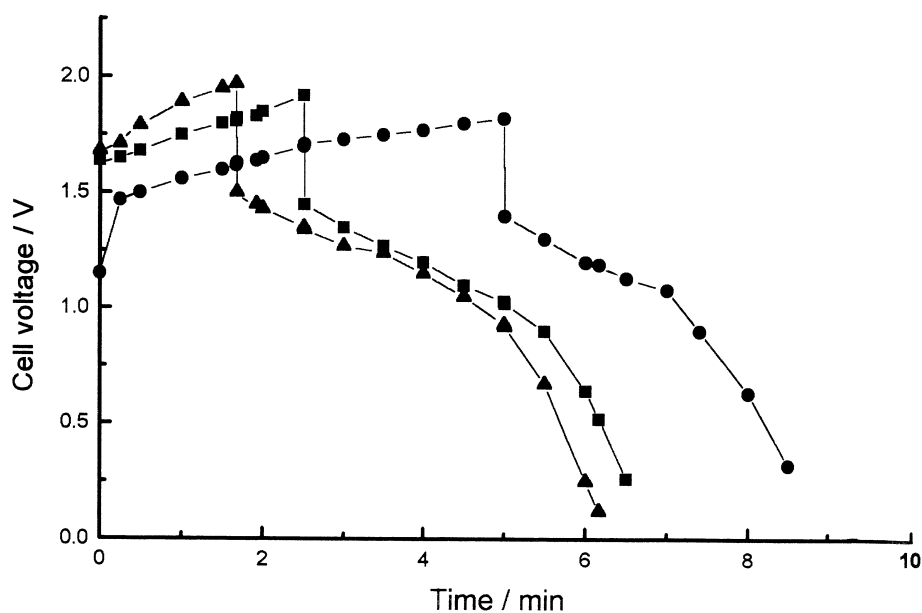


Fig. 4. Charge–discharge curves of the polythiophene on GC/LiClO<sub>4</sub>, Zn(ClO<sub>4</sub>)<sub>2</sub>, PC/Zn battery. Discharging was done always at a current density of 0.16 mA cm<sup>-2</sup> to 47 mC cm<sup>-2</sup>. Charging current density: (●) 0.16, (■) 0.31, (▲) 0.48 mA cm<sup>-2</sup> (total film capacity  $Q_s = 0.95 \text{ C cm}^{-2}$ ).

Figure 4 shows charge–discharge curves when the charging current varies and the discharge rate is constant. The final cell voltage of the charged cell was found to be only slightly dependent on the charging rate, in contrast to certain all-polymer batteries [7]. From Fig. 4 when the charging rate is doubled, the final voltage increases roughly for 100 mV.

The coulombic efficiency as a function of the charging rate is presented in Table 4. The coulombic efficiency is slightly improved by the increase in charging rate. The explanation of this unusual behaviour is found in the cyclic voltammograms presented in Fig. 1 which indicate that the diffusion controlled polythiophene oxidation is superimposed upon a secondary irreversible process, manifesting itself as a current jump when the polarization approaches its final anodic value. The secondary process probably relates to solvent oxidation on polythiophene, and causes the charge loss, as has been proved by increasing the anodic potential and reversing the process. The shape of the voltammograms in Fig. 1 is determined preferably by the polythiophene oxidation, since the peak current is proportional to the square root of the polarization rate. On the other hand, for the secondary process alone in the same polarization range, as expected

Table 4. Coulombic efficiency at various charging rates for the PT/Zn cell at room temperature

Charge rate/ $\mu\text{A cm}^{-2}$	Coulombic efficiency/%
160	90
310	97
480	98

Discharging rate: always 0.16 mA cm<sup>-2</sup>; charging: up to 47 mC cm<sup>-2</sup>.

from the theory of voltammetry of irreversible processes [8], the voltammogram is much less sensitive to the changes in polarization rate. Therefore, with increase in polarization rate, the charge consumed by the secondary process is expected to show a diminishing contribution to the total charge consumed. If applied to battery tests involving charging rate variation, this should lead to an improvement in coulombic efficiency with increase in polarization rate.

#### 4. Conclusions

The charge–discharge characteristics of the battery PT on GC/1.0 M LiClO<sub>4</sub>, PC, 0.1 M Zn(ClO<sub>4</sub>)<sub>2</sub>/Zn with a polythiophene cathode were examined. The average discharge voltage was found to be approximately 1.2 V. In the region of low current densities the coulombic efficiency was higher than 95% independently of discharging rate, but in the fast charge–discharge regime, the coulombic efficiency decreased with increasing discharge rate.

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