

## KINETICS OF SEMICONDUCTING POLYMER ELECTRODES IN LITHIUM CELLS

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### Summary

Recently, there has been a growing interest in semiconducting polymers as electrodes in rechargeable lithium batteries. A number of polymers have been proposed for this important application. The impact these new electrode materials have on lithium battery technology, however, has not yet been fully ascertained. In an attempt to clarify this aspect, we have examined the electrochemical behaviour of some of the most promising semiconducting polymers, namely, polyacetylene, polythiophene, polydithienothiophene and polypyrrole.

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### Introduction

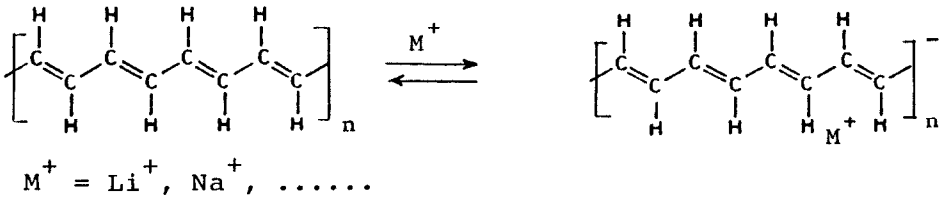
Much attention has been devoted, recently, to the possibility of using conducting polymers as electrodes in advanced, high-energy batteries and several polymeric materials have been proposed for this use. Various polymers can be oxidized or reduced electrochemically by polarizations in suitable cells: in this way, the charge which is removed from, or injected into, the polymeric chains, is balanced by a negative (or positive) counterion from the electrolytic solution. Figure 1 illustrates some schemes of oxidation and reduction processes related to common polymer electrodes, *i.e.*, polyacetylene (PA), polypyrrole (PPy) and polythiophene (PT).

The electrochemical processes of Fig. 1 are often referred to as 'doping' processes, either of p-type or of n-type, by a direct use of the common semiconductor terminology. The electronic processes which are involved in the case of organic polymers, however, are quite different from those concerning classical semiconductors, and thus the term 'doping' may be some-

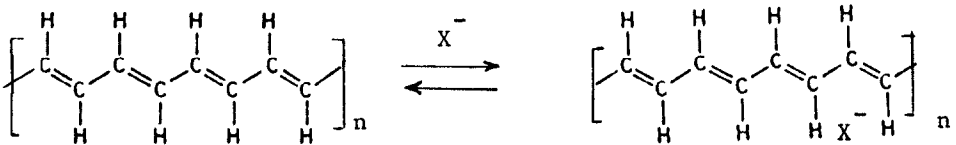
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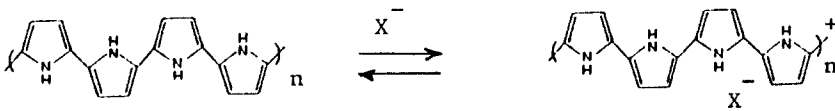
POLYACETYLENE (reduction or 'n-doping'):



POLYACETYLENE (oxidation or 'p-doping'):



POLYPYRROLE (oxidation or 'p-doping'):



POLYTHIOPHENE (oxidation or 'p-doping'):

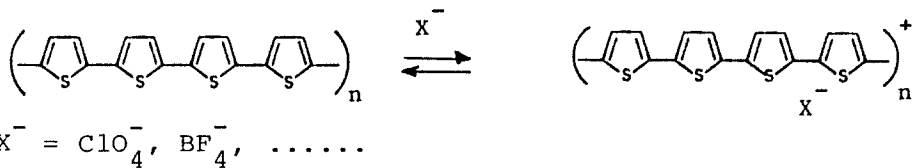


Fig 1 Schemes of the electrochemical redox processes of polyacetylene, polypyrrole and polythiophene

what misleading [1]. Processes of the type illustrated in Fig. 1 may be more correctly classified as redox reactions [1] rather than doping reactions.

These redox reactions are generally reversible and this, in principle, allows the use of the polymers as electrodes, either positive (oxidation

reaction) or negative (reduction), in batteries and related electrochemical devices. To be effective, however, applications of this type require that the electrochemical redox processes fulfill the following requirements: (i) fast kinetics (to ensure high rates), (ii) reversibility (for high coulombic efficiency); (iii) cyclability; (iv) stability (to provide a long shelf-life), (v) high energy density (to be competitive).

In this paper we examine the electrochemical behaviour of some common polymers, *i.e.*, PA, PPy, PT and polydithienothiophene (PDTT), in respect of the above listed requirements in an attempt to assess their possible effectiveness in rechargeable lithium batteries. This analysis is based on results obtained with cyclic voltammetry (CV), frequency response analysis (FRA), charge-discharge (C-D) cycles and absorption spectra (AS).

## Experimental

The chemical and the electrochemical syntheses of the polymer samples, as well as the preparation of the electrolytic solutions and of the electrochemical cells, have been described in detail previously, [2 - 8].

## Results and discussion

### *Polyacetylene*

Figure 2 shows the repetitive CV of the oxidation process of PA in lithium perchlorate-propylene carbonate (1 M LiClO<sub>4</sub>-PC) electrolyte:



The trend of the curves in Fig. 2 indicates that the process is limited by poor cyclability and by low efficiency; the cycles are not reproducible and the shape of the curves deteriorates upon cycling. Furthermore, the PA electrodes are not stable, showing self-discharge upon storage in the organic electrolyte (Fig. 3) [2, 5].

These kinetic and stability limitations may be explained on the basis of a slow diffusion of the ClO<sub>4</sub><sup>-</sup> counterion from the bulk of the polymer to the interface [4, 9, 10]. Only those counterions which are in the proximity of the surface of the polymer electrode are easily exchanged. This induces a low charge-discharge efficiency, which decreases when the electrode is stored in its charged state, thereby allowing the diffusion of a progressively increasing number of counterions from the surface to the bulk of the polymer [4].

This interpretation, based on diffusion-controlled kinetics, is, in part, confirmed by the Warburg-type behaviour at low frequency, shown by the FRA of a PA(ClO<sub>4</sub>)<sub>0.01</sub> electrode (Fig. 4). Effectively, the diffusion coefficient of X<sup>-</sup> counterions (*e.g.*, X<sup>-</sup> = ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, ...) has been reported to be very low, ranging between 10<sup>-18</sup> and 10<sup>-15</sup> cm<sup>2</sup> s<sup>-1</sup> at room temperature [11, 12]

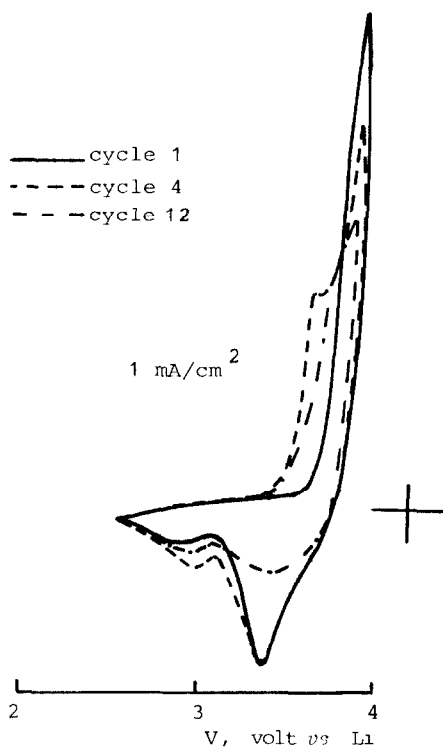


Fig 2 Repetitive cyclic voltammetry of a PA electrode in the  $\text{LiClO}_4\text{-PC}$  electrolyte [2]  
Scan rate  $0.4 \text{ mV s}^{-1}$

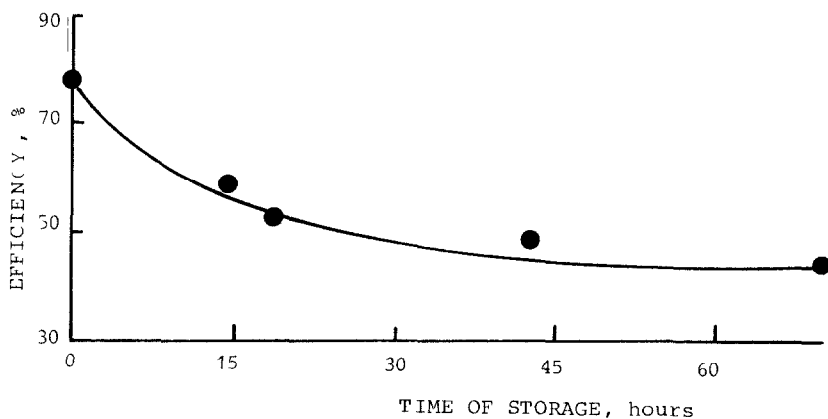


Fig 3 Changes of charge-discharge efficiency of a  $\text{PA}(\text{ClO}_4)_n$  electrode vs time of storage (in the charged state) in the  $\text{LiClO}_4\text{-PC}$  electrolyte [2] Li counter electrode

In conclusion, the slow diffusion of the counterion  $\text{X}^-$  seems to limit the kinetics of the electrochemical process of PA and thus its possible application as a positive electrode in high-rate, lithium batteries

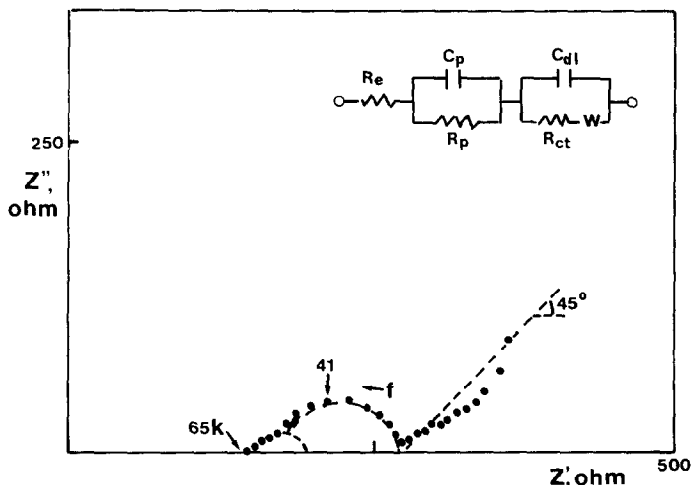


Fig 4 Impedance plot of a  $\text{PA}(\text{ClO}_4)_{0.01}$  electrode after storage in the  $\text{LiClO}_4$ -PC electrolyte for 14 h [4] Li counter electrode

With regard to the energetic content, one has to consider that, in general, the energy density of polymer electrodes is directly related to the extent of the oxidation reaction or, as commonly referred to, to the 'doping level'  $n$ . The higher the value of  $n$  the higher the capacity and, thus, the energy density.

In the case of  $\text{PA}(\text{ClO}_4)_n$  electrodes, the maximum values of  $n$  range around 10% (per CH unit) and this limits the theoretical capacity to  $78 \text{ A h kg}^{-1}$  and, assuming an averaging operating voltage of 3 V, the theoretical energy density to  $230 \text{ W h kg}^{-1}$ , based on the weight of active materials only.

A similar situation applies for the reduction process of PA, even if slightly faster kinetics and better reversibility are observed [13, 14], due to the fact that the diffusion in the polymer of the  $\text{M}^+$  counterion (here  $\text{Li}^+$ , see Fig. 1) is slightly higher than that of  $\text{X}^-$ .

#### *Polythiophene and polydithienothiophene*

Figure 5 illustrates the CV of the oxidation process of polythiophene (PT) in  $\text{LiClO}_4$ -PC, DME (DME: dimethoxyethane):



The anodic and cathodic cycles have similar shape and the integrated charge under the oxidation waves,  $Q_a$ , is very similar to that under the reduction wave, reflecting a coulombic efficiency,  $\eta$ , which approaches 100%.

Very fast kinetics and good cyclability are also shown by PDTT [6], which is characterized by the following oxidation process:



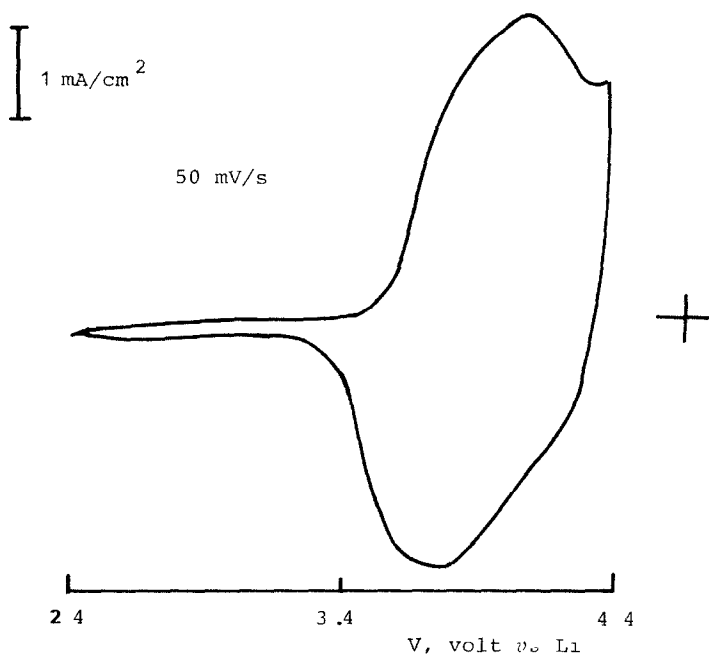


Fig 5 Cyclic voltammogram under steady state conditions of a PT electrode in the  $\text{LiClO}_4\text{-PC}$ , DME solution [7] Scan rate  $50 \text{ mV s}^{-1}$  Li counter electrode

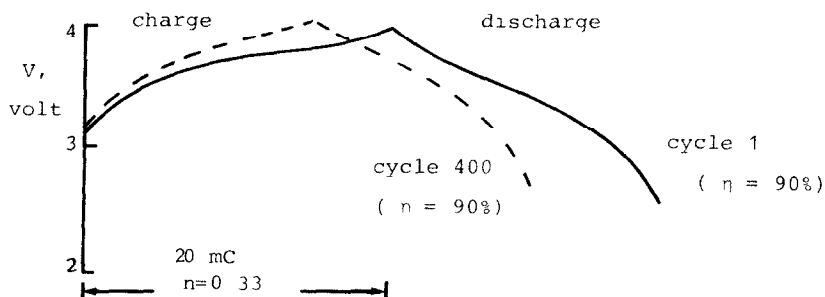


Fig 6 Charge-discharge cycles of a  $\text{Li/LiClO}_4\text{-PC/PDTP}(\text{ClO}_4)_n$  cell at room temperature [6]

These results indicate that thiophene-based electrodes are not affected by those diffusion problems which limit the kinetics of PA electrodes [6, 7]. Indeed, good C-D cycling behaviour is obtained for an  $\text{Li/LiClO}_4\text{-PC/PDTP}(\text{ClO}_4)_n$  cell (Fig. 6)

PT and PDTP electrodes, however, suffer self-discharge problems which induce a rapid loss of electrochemical activity when stored in the charged state in the organic electrolyte. This is clearly shown by Fig 7 which gives the absorption spectra of a  $\text{PT}(\text{ClO}_4)_n$  film deposited on an  $\text{SnO}_2$ -coated glass substrate. The spectrum of a freshly charged electrode shows the typical bands of the 'doped' state. Upon storage in the  $\text{LiClO}_4\text{-PC}$  electrolyte, the spectrum progressively changes (see curve 3), to reveal finally

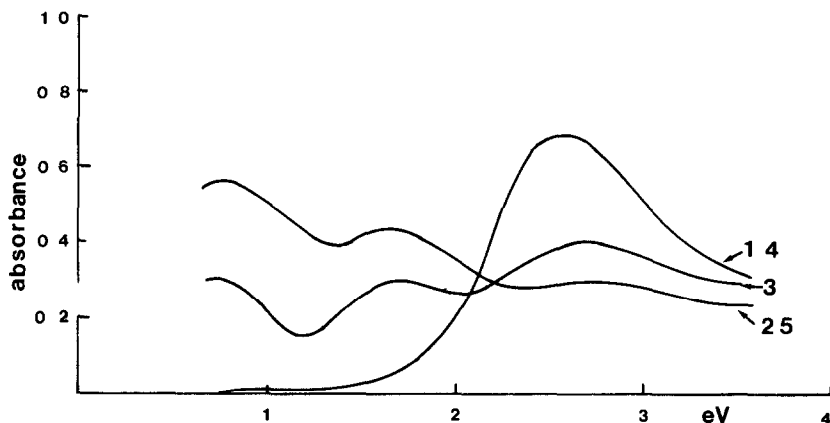


Fig 7 *In situ* absorbance spectra of the  $\text{PT}(\text{ClO}_4)_n/\text{SnO}_2$  electrode ( $\Gamma = 6 \times 10^{-7}$  thiophene mole/cm<sup>2</sup>) in  $\text{PC-LiClO}_4$  1, 'undoped' electrode, 2, immediately after charge (doping level 0.16 per thiophene ring), 3, after storage in the  $\text{LiClO}_4\text{-PC}$  electrolyte for 70 min, 4, after storage for 17 h, 5, electrochemically regenerated doped electrode ( $n = 0.16$ ), immediately after charge

only the band of the 'undoped' state (see curve 4). This self-discharge process is not accompanied by an irreversible polymer degradation, since the charged (doped) state may be fully regenerated by an electrochemical step (see curve 5).

It is difficult to explain the mechanism of the self-discharge process, since the reduction (undoping) of the electrode must be accompanied by an oxidation process whose nature is still unknown. One hypothesis is that the oxidation process may involve the solvent and/or impurities in the electrolyte solution [6].

PDTT electrodes have an attractive capacity content, since the 'doping level' may be extended up to 50% (per thiophene ring). The applicability of this conductive polymer, however, appears to be subordinate to the solution of the self-discharge phenomena.

### Polypyrrole

Figure 8 shows the CV of the oxidation process of PPy in the  $\text{LiClO}_4\text{-PC}$  electrolyte:



Under steady state conditions, the electrode may be cycled many times with a coulombic efficiency which approaches 100% [8]. Therefore, the kinetics of the PPy electrode also appear faster than those of PA electrodes. The frequency response (Fig. 9), however, reveals a Warburg behaviour at low frequency, which would indicate that, under extreme conditions, the performance of the PPy electrodes may also be affected by the diffusion of the  $\text{ClO}_4^-$  counterions within the bulk of the polymer. The faster kinetics and higher reversibility shown by the CV curves, however, indicate that the

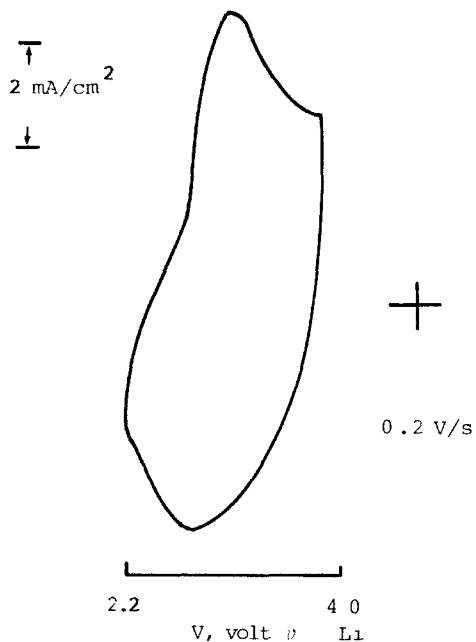


Fig 8 Repetitive cyclic voltammetry of a PPy electrode in the LiClO<sub>4</sub>-PC electrolyte [8] Scan rate 50 mV s<sup>-1</sup> Li counter electrode

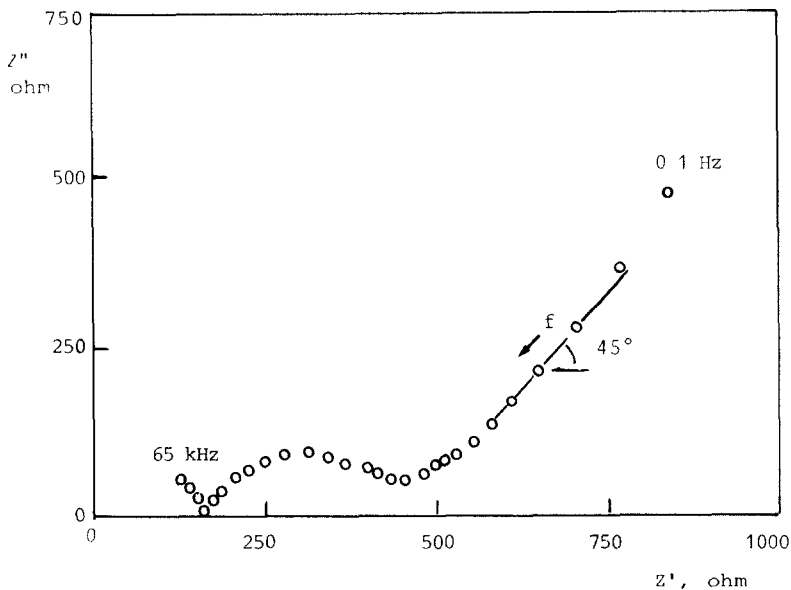


Fig 9 Impedance plot of the PPy(ClO<sub>4</sub>)<sub>n</sub> electrode in the LiClO<sub>4</sub>-PC electrolyte [8] Li counter electrode



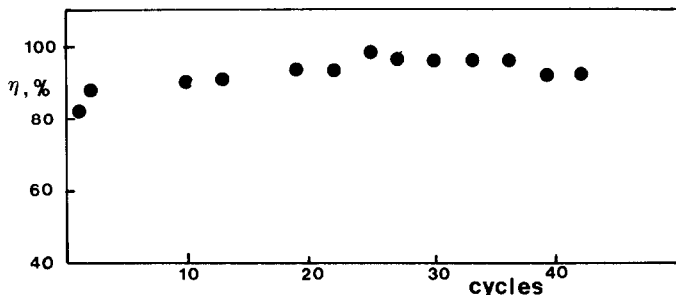


Fig 10 Cycling charge-discharge efficiency of a  $\text{Li/LiClO}_4\text{-PC/PPy(ClO}_4)_n$  cell [8]

diffusion of  $\text{ClO}_4^-$  is faster in PPy than in PA. Good cycling behaviour is obtained by  $\text{Li/LiClO}_4\text{-PC/PPy(ClO}_4)_n$  cells, as illustrated by Fig. 10 which gives the values of charge-discharge coulombic efficiency obtained upon cycling.

Absorption spectra of  $\text{PPy(ClO}_4)_n$  electrodes in contact with the organic electrolyte [15] reveal that the extent of the self-discharge is much less in these electrodes than in other polymers (*i.e.*, limited to approximately 25% of the total stored charge).

PPy electrodes also appear more promising in terms of specific capacity since they are characterized by 'doping levels' which may reach 33% (per pyrrole ring) [10, 16].

## Conclusion

In conclusion, it now appears possible to obtain polymers characterized by fast and reversible electrochemical doping processes. Some questions on their effective applicability in lithium batteries, however, still remain unsolved. One of them is related to the electrochemical stability which, with the possible exception of PPy, seems to be a drawback common to all polymers in their doped state. Another point of concern is the energy content, which is directly related to the doping level achievable with the electrochemical processes. At the moment, all of these aspects make it improbable that there will be a successful utilization of conductive polymers as electrodes for high-rate, long-life lithium batteries.

The field is still very young, however, and new types of conductive polymer electrodes are being continuously characterized and proposed for electrochemical applications. Among the most recent examples are polyphenylene [14] and polyaniline [17]. Therefore, a breakthrough in this important sector of battery technology may be achieved in the near future. This may not necessarily be directed towards high-energy devices but to more specific applications where the unique properties of the polymeric materials may be adequately exploited.

## Acknowledgements

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