

ELECTROCHEMICAL CHARACTERISTICS OF POLYACETYLENE IN ORGANIC ELECTROLYTES

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Summary

The characteristics of the electrochemical doping process of polyacetylene have been investigated in lithium cells using lithium perchlorate in propylene carbonate as the electrolytic solution. The kinetics of this process are controlled by the diffusion of the dopant species throughout the polymer. Therefore, polyacetylene samples with a highly porous, extended surface should be selected for the development of efficient, rechargeable lithium batteries. In line with this, we have considered foam-type polyacetylene electrodes which have a lower density than the 'classical' Shirakawa-type film electrodes. The electrochemical behaviour of the polyacetylene foam samples has been examined by cyclic voltammetry response and constant current, charge-discharge cycles. The results are described in this work.

Introduction

In previous papers [1 - 3] it has been shown that the kinetics of the p-doping electrochemical process of polyacetylene (PA) in organic electrolytes are controlled by the diffusion of the dopant species, which appears to be particularly slow from the bulk to the surface of the polymer. Therefore low rates and poor coulombic efficiencies are to be expected for 'classical', Shirakawa-type PA film electrodes, as, indeed, has been confirmed by the independent results of various authors [4 - 6].

Improvements in the characteristics of the electrochemical process may be obtained by changing the morphology of the polymer electrode. Effectively, foam-type PA electrodes, which have a highly porous surface, may sustain much higher cycling rates and offer much better coulombic efficiencies than film-type PA electrodes, which have a low porosity and a smooth surface [3].

In this paper the electrochemical behaviour of the foam-type PA electrodes in lithium organic electrolyte cells has been further examined by cyclic voltammetry and constant current, charge-discharge cycles.

Experimental

The synthesis of the PA samples and the purification of propylene carbonate (PC) and of lithium perchlorate, LiClO_4 , have been described elsewhere [3]. In particular, foam-type polyacetylene was prepared following the method described by Wnek *et al.* [7]. A three-electrode glass cell was used for the electrochemical tests. The PA working electrodes (approximately 1 cm^2 surface) were sandwiched in a platinum mesh and housed in the central compartment of the cell, while the Li reference and Li counter electrodes, respectively, were located in two side compartments. The lower part of the cell was first filled with a layer of activated alumina and then by approximately 5 cm^3 of the LiClO_4 -PC solution [2]. The electrochemical stability window of this solution, measured in the same cell using the bare platinum mesh as the indicator electrode, is between 2.5 and 4.0 V (*vs.* Li). All the manipulations and the experimental procedures were performed in a controlled atmosphere dry-box (less than 4 ppm of water). Standard electrochemical equipment was used for the cyclic voltammetry and the polarization studies.

Results and discussion

In Fig. 1 the cyclic voltammetry of a typical Shirakawa-type PA film electrode is compared with that of a PA foam electrode, both obtained in the same LiClO_4 -PC electrolyte and with the same scan rate.

The voltammograms reveal two oxidation peaks, at about 3.6 V and 3.8 V, respectively, *vs.* Li, and this implies a two-step mechanism whose nature is not yet fully understood. The two peaks suggest the presence in the basic PA structure of two different sites available for the electrochemical doping process. This mechanism is, in part, supported by recent work of Cernia *et al.* [8] who have shown that the iodine p-doping process of PA occurs in three steps whose rate constants differ by orders of magnitude.

As shown in previous papers [2, 3] and also supported by the results of other authors [5, 6], the kinetics of the electrochemical p-doping process of PA is controlled by the diffusion of the dopant ClO_4^- species throughout the polymer. In particular, it has been demonstrated [9] that the diffusion of ClO_4^- is much faster within the PA fibrils than inside the fibrils. Therefore the behaviour of the PA electrodes should be greatly influenced by this morphology. As shown in Fig. 1, foam-type electrodes, which are characterized by an extended, porous surface, effectively show a much better response, in terms of height, separation and reversibility of the two peaks, than the film-type electrodes, which have a dense, smooth surface.

This difference in behaviour is further illustrated in Fig. 2, which shows two typical constant current, charge-discharge cycles of lithium, LiClO_4 -PC cells using the two types of PA electrodes. While the 'charging' processes are similar, both involving a doping level of about 1.3% (*i.e.*, the formation of

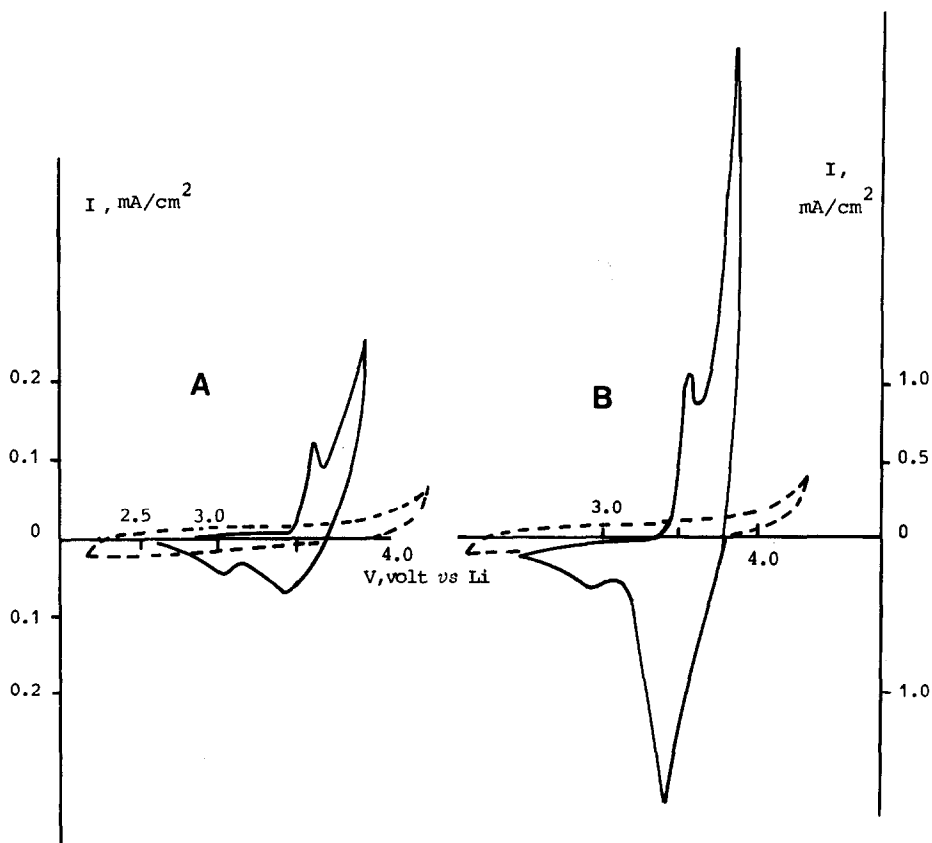


Fig. 1. Cyclic voltammetry of a PA film (A) and a PA foam (B) electrode in the $\text{LiClO}_4\text{-PC}$ electrolyte. - - -, electrolyte only (Pt mesh electrode). Scan rate: 0.4 mV/s.

$[\text{CH}(\text{ClO}_4)_{0.013}]_x$, the overall charge-discharge characteristics reflect the differences already pointed out by the voltammetric responses, *i.e.*, (i) the cell based on the film-type electrode shows a poor coulombic efficiency, *i.e.*, around 50%; (ii) the cell based on the foam-type electrode shows a two-plateau behaviour (especially well defined in the discharge curve) and a higher efficiency, *i.e.*, around 87%.

It must be remarked that a low efficiency seems to be typical of PA film electrodes: it remains around 50% and does not improve upon cycling [1, 2, 6, 10]. It is, then, reasonable to assume that such a low coulombic efficiency may be ascribed to a slow diffusion of the ClO_4^- species from the bulk to the surface of the polymer.

Apparently, only the species on the surface are easily removed using a constant-current process [9], while those which had reached the bulk of the polymer can be 'pulled out' only by an extended, controlled-potential process [2, 3]. Therefore, the slow diffusion of ClO_4^- in PA films hinders the recovery of a large fraction of the stored charge, and this again illustrates the

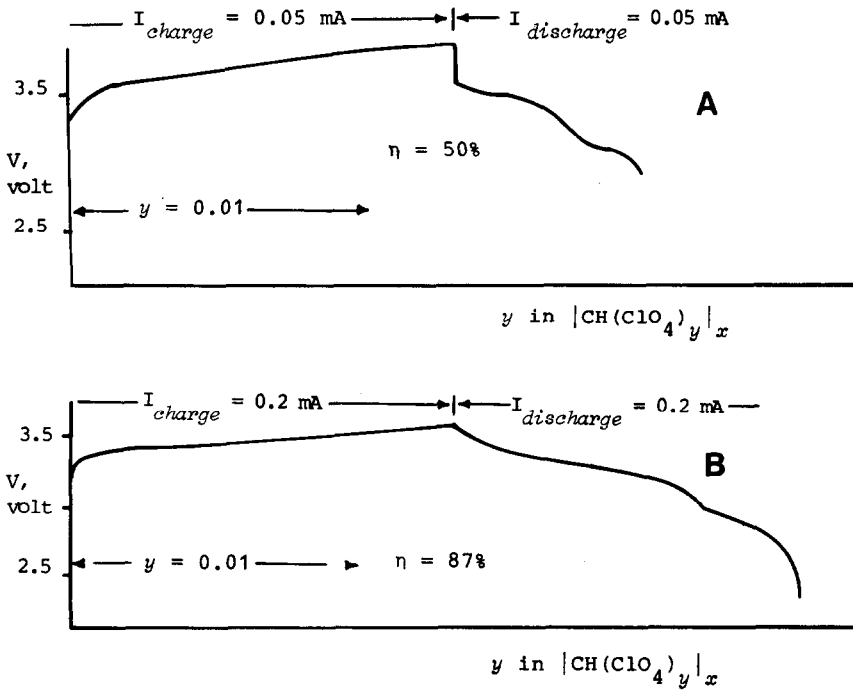


Fig. 2. Typical consecutive constant current charge-discharge cycles of Li/LiClO₄-PC cells using (A) a PA film electrode; (B) a PA foam electrode. Electrode surface: 1 cm².

critical role of the electrode morphology on the characteristics of the electrochemical doping process: the larger the surface area, the better the charge-discharge efficiency.

To confirm this, cyclic voltammograms of PA foam electrodes compressed at different pressures, and thus having different densities, are compared in Fig. 3. The lower the density the higher is the porosity of the electrode: accordingly, the response in terms of separation, height, and reversibility of the peaks, progressively increases.

The cycling characteristics of an Li-PA cell, using a low-density foam sample, are listed in Table 1. The following three main effects may be deduced from these data:

(i) the first cycles have a lower efficiency than the following cycles. This is not uncommon in rechargeable batteries, and in lithium systems in particular. In the case examined here, one may assume that the first dopant species remain strongly bound to the polymer host structure, and thus are not easily removable. These initial species, with a sort of 'activation' mechanism similar to that proposed in intercalation processes [11], would then favour the following charge-discharge cycles, thus enhancing their reversibility;

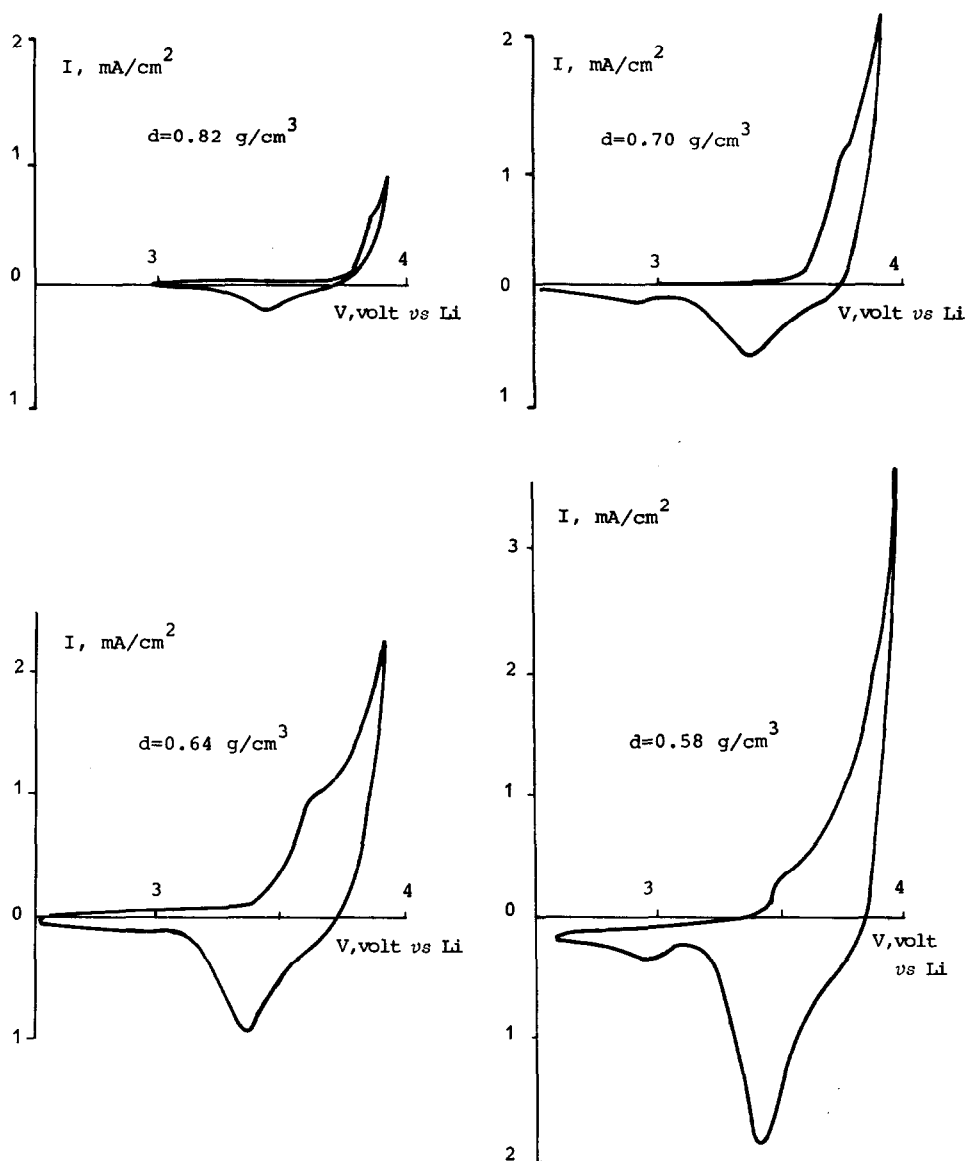


Fig. 3. Cyclic voltammety of PA foam electrodes having different densities in the $\text{LiClO}_4\text{-PC}$ electrolyte. Scan rate: 0.4 mV/s.

(ii) after the three initial cycles, average coulombic efficiencies around 88% are obtained, a value higher than that so far reported for film-type PA electrodes under the same conditions;

(iii) the efficiency of cycle no. 7 is sensibly lower than the average value. This was a prolonged cycle where the doping level during the charge process reached almost 5.5%. Obviously, during this long process a fraction

TABLE 1

Charge-discharge characteristics of an Li/LiClO₄-PC/(CH)_x cell at room temperature. The (CH)_x foam electrode had a density of 0.42 g/cm³ and a surface area of 1 cm²

Cycle no.	I_{charge} (mA)	$I_{\text{discharge}}$ (mA)	y doping level in CH(ClO ₄) _y _x reached with charge (%)	Coulombic efficiency (%)
1	0.2	0.2	1.00	27
2	0.2	0.2	1.00	52
3	0.2	0.2	1.80	56
4	0.2	0.2	2.04	73
5	0.2	0.2	2.22	83
6	0.2	0.2	2.96	75
7	0.2	0.2	5.48	63
8	0.2	0.2	2.60	71
9	0.2	0.5	2.33	71
10	0.2	0.5	3.07	78
11	0.2	0.5	3.00	80
12	0.2	0.5	2.74	86
13	0.2	0.5	2.70	86
14	0.5	0.5	1.70	100
15	0.5	0.5	1.60	100
16	0.5	0.5	1.60	100
17	0.3	0.3	1.87	100
18	0.3	0.3	2.00	98
19	0.3	0.3	1.93	100
20	0.3	0.3	1.87	97
21	0.3	0.3	1.75	100
22	0.3	0.3	1.66	98
23	0.3	0.3	1.26	100

of the dopant species could diffuse towards the bulk of the electrode, thus no longer being available for the subsequent constant current discharge process.

The last observation would also indicate that the foam-type PA electrode may suffer from a poor coulombic efficiency if sufficient time is allowed to reach critical conditions. To confirm this, a slow-rate, repetitive cyclic voltammetry of a low-density PA-foam electrode is shown in Fig. 4. It should be noted first that the second cycle has a better peak definition than the first (Fig. 4(A)), this being in agreement with effect (i). However, as the cycling proceeds, the first peak progressively shifts and the response decays (Fig. 4(B)). After 12 cycles only one oxidation peak is detectable and the overall peak height is greatly reduced.

These results would indicate that only fast, shallow cycles, with no interruption between the charge and the discharge processes, may offer reasonably high coulombic efficiency, since only this type of cycling assures a transfer of the dopant species which remains within the polymer surface.

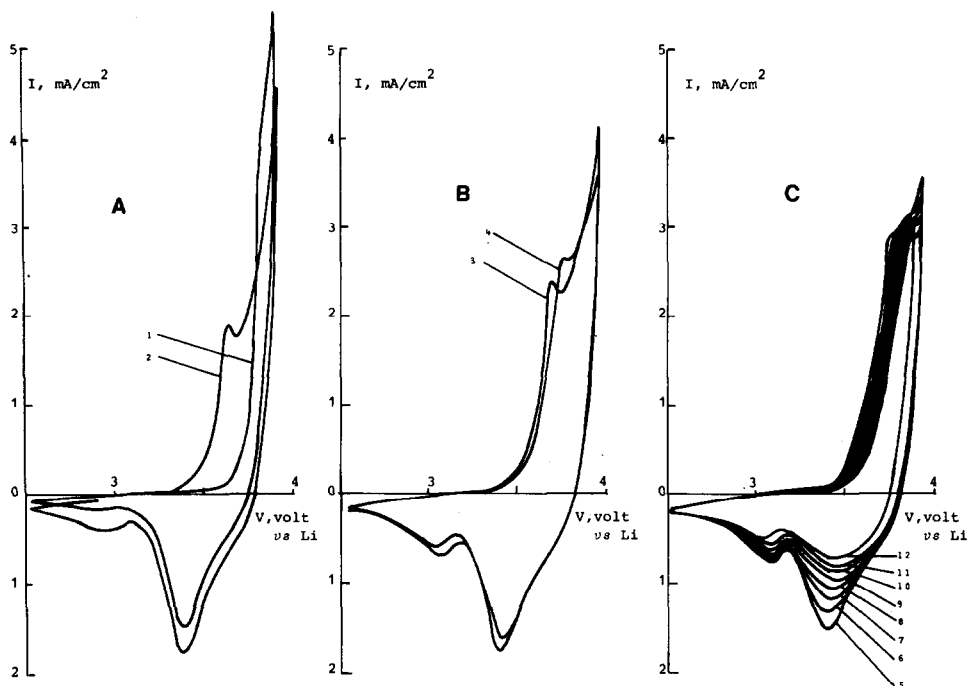


Fig. 4. Repetitive cyclic voltammety of a PA foam electrode in the $\text{LiClO}_4\text{-PC}$ electrolyte. Electrode density: 0.58 g/cm^3 . Scan rate: 0.4 mV/s .

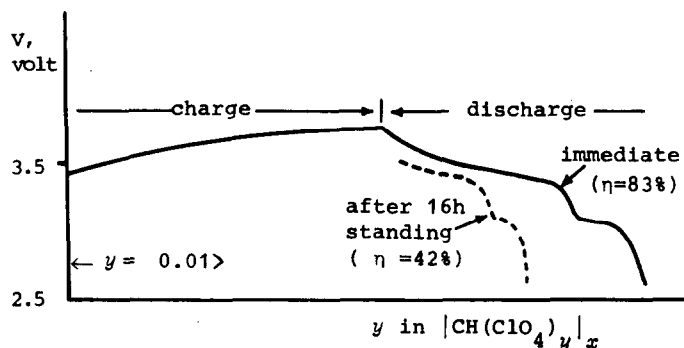


Fig. 5. Immediate and delayed constant current (0.2 mA/cm^2) discharge of a PA foam electrode charged at 0.2 mA/cm^2 to a doping level of 2.2% in a $\text{LiClO}_4\text{-PC}$ electrolyte. PA foam sample density: 0.58 g/cm^3 .

To confirm this, a low-density PA foam electrode was first charged to a doping level of 2.2%. The immediate discharge recovered 83% of the charge. However, when the charged electrode was allowed to stand in the electrolyte for 16 h, the efficiency dropped to 42% (Fig. 5).

Such a 'loss of charge' effect has often been noticed in classical Shirakawa-type PA film electrodes where it has been attributed to a self-discharge process or even to an irreversible chlorination of PA by ClO_4^- [2]. In the light of the results presented here, it appears that the effect is more likely ascribable to the difficulty of removing the dopant species which, upon standing, had moved into the bulk of the polymer structure.

One may, then, conclude that a highly porous surface morphology should certainly be preferred for polyacetylene if it has to be used as an electrode in rechargeable lithium batteries. The choice of the foam samples described here is a preliminary step in this direction. The foam PA electrodes behave better than the more common film electrodes, but they still present the same basic problems connected with the slow diffusion of the dopant species. Other solutions, either directed to the optimization of the electrolyte or to optimization of the polymer morphology, or to a combination of both, must be sought for the final answer.

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