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SHORT COMMUNICATION

Electrochemical behaviour of polypyrrole films as secondary battery electrodes in $LiClO_4$–propylene carbonate*

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1. Introduction

In recent years there has been a great interest in the utilization of conductive polymers as secondary battery electrodes. The prototype of these polymers is polyacetylene which has been extensively investigated as a positive electrode in lithium batteries [1–5]. The main problem with using polyacetylene as an electrode material is its poor stability in the presence of oxygen and water [6].

Polyparaphenylene is stable in its neutral form and the doped polymer can be employed as a rechargeable battery electrode in conjunction with lithium metal [7]. The open circuit voltage of this battery is very high (4.4 V) and the solvent is unstable under the charge–discharge conditions of secondary batteries.

Polypyrrole (PP) films (obtained by electropolymerization of pyrrole in acetonitrile solutions) are very stable [8]. The thinner films ($< 1\ \mu m$) can be repeatedly oxidized and reduced with no apparent change in the material. The use of these films in many electrode applications is very attractive because they can be readily prepared from commercially available chemicals in a simple procedure. The application of polypyrrole as the cathode of rechargeable lithium batteries is possible in principle, but there are some unresolved questions that must be studied before a commercial use of this material can be considered. We are reporting here on the synthesis and electrochemical behaviour of polypyrrole in $LiClO_4$–propylene carbonate (PC) focusing on practical aspects of its possible use as a cathode in lithium cells.

2. Experimental procedure

Polypyrrole films were electrochemically deposited on platinum from solutions containing 0.1 M pyrrole and 0.1 M $LiClO_4$ in PC. A platinum wire was used as the counter electrode and Ag–AgCl/3 M LiCl in ethanol as the reference electrode. The chemicals were all used as supplied (Fluka) without further purification. The solution was continuously degassed with argon. The film thickness was controlled by applying a constant current density ($1\ mA\ cm^{-2}$) for a certain period of time ($0.24\ C\ cm^{-2}$ to obtain a film approximately $1\ \mu m$ thick).

After the electrochemical synthesis the electrolyte was changed to 0.1 M $LiClO_4$–PC solution to carry out the electrochemical experiments. Cyclic voltammograms were made by controlling the potentiostat (Wenking LB.75) with a programmer (PAR 175) and recording the current in a X–Y recorder (Hewlett Packard 7045 A). Impedance measurements were made using a frequency response analyser (Solartron 1250) coupled with an electrochemical interface unit (Solartron 1186). Battery experiments were performed in the same electrochemical cell employed to obtain the polymer, but using aluminium as the counter electrode. All measurements were made at room temperature (20 ± 2° C).

3. Results and discussion

3.1. *Cyclic voltammograms*

After the electrochemical deposition, the

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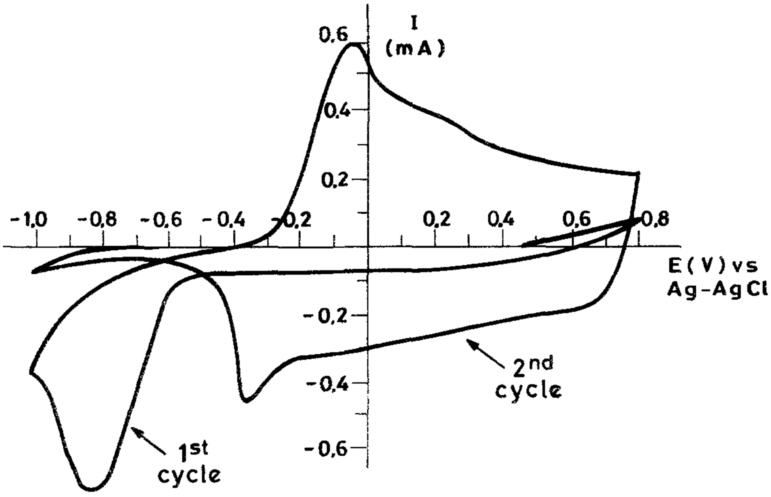

Fig. 1. Cyclic voltammetry of polypyrrole in 0.1 M $LiClO_4$–propylene carbonate. Film thickness, ~ 1 μm; scan rate, 20 mV s^{-1}.

polypyrrole films were cycled in 0.1 M $LiClO_4$–PC electrolyte. The scan rate (as a function of the film thickness) and the potential interval (-1.0 V to $+0.8$ V versus Ag–AgCl) were selected to obtain a complete reduction of the polymer within the stability range of the electrolyte.

Fig. 1 shows the voltammograms obtained for a polypyrrole film of ~ 1 μm thickness. As the polymer was already doped, the reduction peak in the first cycle (-0.8 V) corresponds to the undoping of the polymer as follows:

$$[(C_4H_3N)^{+y}(ClO_4^-)_y]_x + xye$$
$$+ xyLi^+ \rightleftarrows [C_4H_3N]_x + xyLiClO_4$$

The integration of the peak gave a value of $y = 0.33$ in agreement with the previously reported doping level [12] and the elemental analysis of a ~ 10 μm film (C = 46.6%, H = 2.7%, N = 12.5%, Cl = 10.1%).

After the first scan, reproducible voltammograms were obtained with an oxidation peak (doping) at -0.1 V and a reduction peak (undoping) at -0.3 V. At positive potential, the quasi-constant current density (i_c) obtained is proportional to the scan rate (V) and immediately changes sign when the scan is reversed. The equivalent capacitance, measured from i_c/V (~ 0.02 F cm^{-2}) is three orders of magnitude greater than that of the metal in this electrolyte and is proportional to the film thickness. The behaviour observed is similar to that of a capacitor with very high capacitance and is due to the highly porous structure of polypyrrole films [9, 11].

The reduction peak in the first cycle is very different from that of the following cycles. The peak potential is much more negative and the peak current is of greater magnitude. A possible explanation could be a change in the dopant anion of the electrochemically cycled films [10]. Nevertheless the elemental analysis of a ~ 10 μm cycled film is essentially the same as that of a fresh film (C = 48.5%, H = 3.4%, N = 12.8%, Cl = 10.1%). So the dopant anion is ClO_4^- in both cases, but the interaction with the polymer is different after cycling. Increasing the film thickness (> 10 μm) the reduction of the polymer becomes much more difficult and slower scan rates are required to undope the polypyrrole films. There is a slow ionic diffusion of the dopant anion in the polymer that could be a serious limitation in high power batteries.

The polymer films are very stable between -1.0 V and 0.8 V versus Ag–AgCl. It is possible to obtain more than 1000 cycles in thin films (< 1 μm) with no change in the coulombic capacity of the electrode. The oxidation and reduction charge in each cycle is the same and does not depend on the scan rate. The peak height is proportional to the scan rate as is expected for a reversible surface process. However, when the upper limit is taken more positive, there is a progressive loss of capacity and film deterioration takes place after a few cycles.

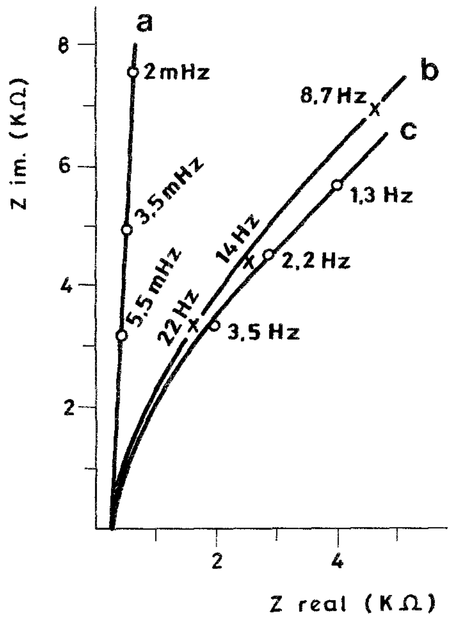

Fig. 2. Analysis of a.c. impedance of polypyrrole (PP) films. Curve a, platinum–polypyrrole (+0.2 V versus Ag–AgCl); curve b, platinum–polypyrrole (−1.0 V versus Ag–AgCl); curve c, platinum alone.

3.2. *Impedance analysis*

Fig. 2 shows the impedance of a cycled polypyrrole film (~ 1 μm) in the supporting electrolyte. At low frequencies (< 1 Hz) and positive potentials, the behaviour is similar to a capacitor with very high capacitance (0.02 F cm^{-2}) in agreement with the large background current observed in cyclic voltammetric studies.

At negative potentials (−1.0 V) in which the polypyrrole film is not conducting, the capacitance decreased by several orders of magnitude (~ 3 μF cm^{-2}). The capacitance observed for bare platinum in the electrolyte (~ 20 μF cm^{-2}) is greater than that of the reduced film showing that the platinum surface is partially blocked by the non-conducting reduced polypyrrole film.

3.3. *Battery experiments*

A LiAl–polypyrrole battery has been made by the deposition of polypyrrole in the positive electrode (platinum) and lithium in the negative (aluminium) of the following electrochemical cell:

$$(+)\ \mathrm{Pt/LiClO_4\text{–}PC/Al}\ (-)$$

Fig. 3 shows the first charge or 'formation' of this battery at a current density of 1 mA cm^{-2}. The polypyrrole film thickness can be varied by controlling the deposition time (3 h to obtain a ~ 0.05 mm film). The open circuit voltage of the battery is 3 V. The discharge current at 0.2 mA cm^{-2} (Fig. 3) is very flat with a mean discharge

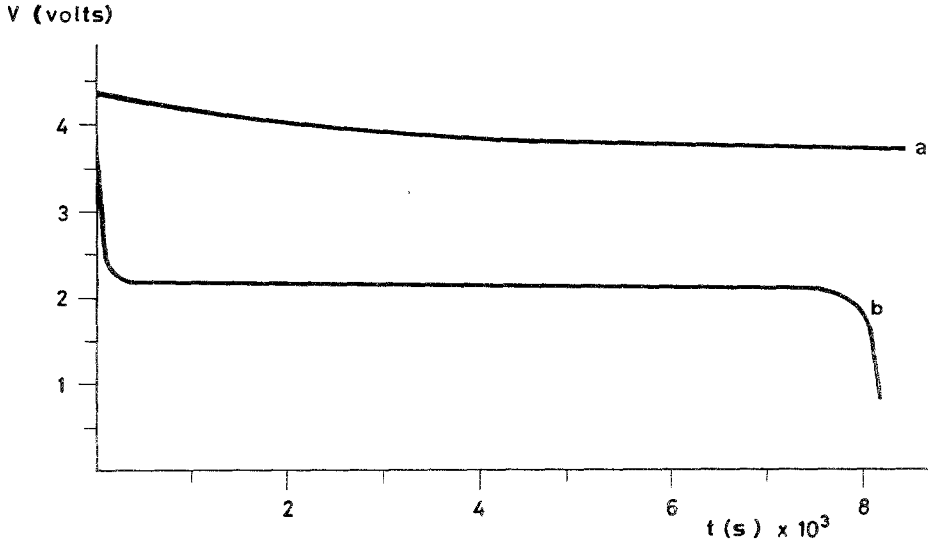

Fig. 3. Discharge curve of LiAl/LiClO$_4$–PC/PP battery. Curve a shows formation at 1 mA cm^{-2}; curve b shows discharge at 0.2 mA cm^{-2}.

voltage greater than 2 V. The theoretical energy density is about 0.2 Wh g^{-1}. In the absence of rest periods between charge and discharge, coulombic efficiency is better than 90%. Cycle life and shelf-life, however, have been found very poor. There is a decrease of cell capacity with cycling (it lost ~ 70% of the initial capacity after 50 deep discharge cycles) and and at open circuit (~ 50% loss on standing overnight).

To make possible the utilization of polypyrrole as a cathode in rechargeable lithium cells it would be necessary to increase the capacity (doping level) and decrease the losses in cycling and at rest that have been observed in this material.

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