

Short Communication

Behaviour of iron polythiophene positive electrodes in lithium cells

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Abstract

A simplified method for electropolymerisation of thiophene at a cylindrical iron cathode is described. Picric acid in aqueous DMSO is found to be an efficient dopant for electropolymerisation. Polythiophene, so formed, is chemically stable both in propylene carbonate (PC) and in mixed PC and dimethylformamide (DMF). The performance characteristics of a cylindrical AA-size cell, formed by coupling an iron polythiophene cathode with a lithium anode are studied using a saturated solution of lithium picrate either in PC or in mixed PC (60 wt %) + DMF (40 wt %) as electrolyte. The open-circuit voltage, short-circuit current and the discharge behaviour of the cell in the mixed solvent are found to be superior to those of the cell using PC as solvent. The results are explained in terms of higher solubility and ion conductivity in the mixed media due to the cation-solvating propensity of DMF.

Introduction

Further to our earlier studies on polypyrrole [1, 2] and polyaniline [3] electrodes, we report here parallel studies with polythiophene electrodes. The scientific and technological importance of these modified electrodes has been described elsewhere [1-7]. Although electropolymerisation of thiophene on gold [6] and platinum electrodes [4] has been investigated, little attention has been paid to achieving the direct formation of a good adherent film on low-cost metals that are suitable for commercial batteries. Nevertheless, polythiophene has been deposited as a secondary coating on polypyrrole primary coatings [5]. Thus, the major objectives of the present work are to report optimum conditions for producing strongly adherent electrodeposition of polythiophene on a cylindrical iron electrode, and to examine the performance characteristics of a cell formed by this iron polythiophene cathode and a lithium anode using two different electrolytes.

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Experimental and results

Thiophene (Fluka, Switzerland) was dissolved in aqueous dimethyl sulfoxide (DMSO 20 wt %) (BDH) containing saturated picric acid (Glaxo) as electrolyte. This solution was placed in a cylindrical AA-size iron cell [8]. The latter was previously etched with dilute HCl, washed repeatedly with distilled water and, finally, the inner surface of the cylinder was rubbed with emery paper. Electropolymerisation was carried out using this iron cylindrical vessel as an anode and a platinum wire as a cathode. Polythiophene (PT) deposition was carried out for 3 to 3.5 h at 3.0 V versus Ag/Ag^+ , a voltage that is almost double the oxidation potential of thiophene. This procedure was adopted in order to achieve a large current density. The preparation of lithium picrate and the purification of DMSO have been described earlier [7]. The PT-coated iron was used as a cathode for a lithium battery. A lithium rod (E. Merck, F.R.G.) of size 0.80 cm (dia) \times 4 cm (length) was employed as the anode. The surface was degreased by treatment with dry-distilled acetone and the oxide coating was removed with a sharp nickel knife under an argon atmosphere. The rod was wrapped in a cotton separator and placed inside the iron cylinder.

Two of the above cells were prepared. The first was charged with a saturated lithium picrate solution in PC, the second cell with saturated lithium picrate solution in a mixed solvent of PC (60 wt %) and DMF (40 wt %). The open-circuit voltage (OCV) and the short-circuit current (SCC) were measured with a digital multimeter (MIC-6E, made in Taiwan) and are given in Table 1. Both the cells were discharged under a drain of 0.5 mA to a cut-off voltage of 1 V. The discharge behaviour of the cells is displayed in Fig. 1. Charging of the cells was carried out at 4 mA for 20 h using a 6 V d.c. power pack. The cells were rested for 1 h and then the OCV and SCC values were measured (Table 1).

Discussion

Difficulties associated with the electrodeposition of polythiophene have been discussed previously [5, 6]. These are probably due to the fact that

TABLE 1

Electrochemical parameters of cells comprising a polythiophene (PT) coated iron cathode and a lithium anode

	Fresh cell		Charged cell	
	OCV (V)	SCC (mA)	OCV (V)	SCC (mA)
Cell I ^a	3.15	2.25	2.87	2.20
Cell II ^b	3.36	11.0	3.31	7.0

^a Li/Li picrate in PC/PT-Fe

^b Li/Li picrate in PC + DMF/PT-Fe

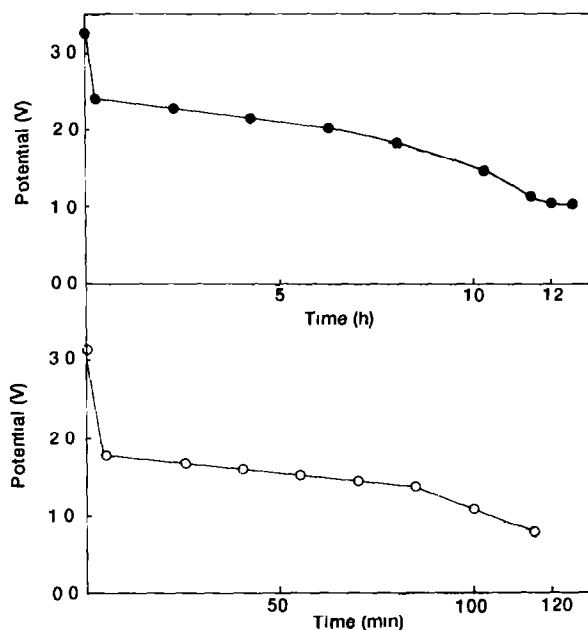


Fig 1 Discharge at 0.5 mA of (—○—) cell I, (—●—) cell II

the common dopants are unsuitable for deposition on substrates other than noble metals. We have noted [2, 3] that picric acid is highly efficient for the electrodeposition of polypyrrole on different substrates. Electrodeposition of polythiophene occurs, however, only when the aqueous medium is replaced by an aquo-organic medium. Aqueous DMSO (20 wt %) has been found to be an ideal mixed solvent for polythiophene deposition using picric acid as dopant. This is probably due to the fact that, in aqueous DMSO, the solubility and conductance of picric acid are both increased. Polythiophene films, so formed, have thicknesses between 20 and 30 μm , and conductivities between 2 and 5 S cm^{-1} .

The polythiophene films were found to be chemically stable in PC and in the mixed solvent of 60 wt % and 40 wt % DMF. The use of such electrodes as rechargeable cathode materials in lithium cells is of special interest. The superior performance of the cell in the mixed solvent is probably due to the higher solubility of lithium picrate [9]. The overall performance characteristics of iron polythiophene positive electrodes in lithium battery systems is found to be satisfactory.

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