

Short communication

Lithium–Polymer battery based on polybithiophene as cathode material

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Received 7 July 2005; accepted 27 October 2005

Available online 10 January 2006

Abstract

Stainless-steel mesh electrodes coated with polybithiophene, obtained by electrochemical polymerization (constant potential and constant current), have been investigated as cathode materials in a lithium–polybithiophene rechargeable battery by cyclic voltammetry, electrochemical impedance spectroscopy and long-term charge–discharge cycling process. The effects of different growth methods on the surface morphology of the films and the charge–discharge capacity are discussed in detail. The results show that polybithiophene-hexafluorophosphate is a very promising cathode material for manufacturing lithium–polymer rechargeable batteries with a highly stable discharge capacity of 81.67 mAh g⁻¹ after 50 cycles.

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Keywords: Bithiophene; Electrochemical deposition; Cathode materials; Capacity; Stainless-steel; Lithium–polymer battery

1. Introduction

The development of new cathodic materials for rechargeable lithium batteries is necessary in order to minimize the processes responsible for the loss of recharge–discharge capacity on charge–discharge cycling. Recently, the use of organic conducting polymers as positive electrode materials in rechargeable batteries has attracted extensive studies [1–5]. Organic conducting polymers are a broad class of π -conjugated polymeric materials that can be easily electrodeposited on to the surface of metallic and semiconductor electrodes [6,7].

In our previous studies [8,9], the use of polypyrrole (PPy) deposited on to different substrates as cathodic materials for lithium–polymer batteries has been found to present interesting and promising applied results with a high discharge capacity associated with very high electrochemical stability during multiple charge–discharge cycles during the charge–discharge process, however, the PPy films were partially over-oxidised when cycled between 2.5 and 4.3 V (two-electrode system) in a lithium–PPy battery. Therefore, thiophene-based polymers are of particular interest due to their potential to provide materials with good electrochemical and structural stability, good electri-

cal conductivity, and a high degree of electroactivity in organic electrolytes [10–13].

In this study, bithiophene is selected as polymerization monomer due to its lower oxidation potential and more stable electrochemical and mechanical properties than those of thiophene monomer. Electrodes are prepared by the electropolymerization of polybithiophene on to lightweight and inexpensive stainless-steel mesh and their electrochemical performance as cathodes in lithium–polymer rechargeable batteries is evaluated. In addition to the growth methods, the electrochemical stability and activity of polybithiophene in a lithium–polymer rechargeable battery is investigated.

2. Experimental

2.1. Reagents and materials

2,2'-Bithiophene (BiTh, Alrich), acetonitrile (ACN, Univar, Ajax), dichloromethane (DCM, Univar, Ajax), tetrabutylammonium hexafluorophosphate (TBAPF₆, Fluka), ethylene carbonate (EC, Aldrich) and dimethyl carbonate (DMC, Aldrich) were used as received. The electrolyte in cells was 1.0 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v, provided by Merck KgaA, Germany).

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Stainless-steel mesh was purchased from Metal Mesh Pty Ltd. (Australia) and used as the electrode substrate for fabrication of polybithiophene-hexafluorophosphate (PBiTh/PF₆) film electrodes. Before coating with polymers, the stainless-steel mesh was cut into the required sizes, rinsed thoroughly with acetonitrile, and allowed to dry.

2.2. Electrochemical polymerization and characterization of polybithiophene electrodes

Electrosynthesis and electrochemical characterization of the polymers were performed by means of an electrochemical hardware system that was comprised of an EG&G PAR 363 Potentiostat/Galvanostat, a Bioanalytical Systems CV27 Voltammograph, MacLab 400 with Chart v 3.5.7/EChem v 1.3.2 software (ADInstruments), and a PC computer. A three-electrode electrochemical cell was used and comprised a working electrode (stainless-steel mesh), an auxiliary electrode (carbon paper), and an Ag/Ag⁺ reference electrode (0.01 M AgNO₃ in 0.1 M TBAP/CH₃CN) with a salt bridge (0.1 M TBAP/CH₃CN).

2.3. Scanning electron microscopy (SEM)

The morphologies of the polybithiophene-modified, stainless-steel mesh electrodes were examined with a Leica Model Stereoscan 440 scanning electron microscope (SEM). The SEM examinations were conducted at room temperature under an accelerating voltage of 20 kV.

2.4. Electrochemical ac impedance analysis

Impedance analysis was conducted using a conventional three-electrode configuration. The polybithiophene electrodes were used as the working electrodes, while lithium foils served as both counter and reference electrodes. The impedance was measured with an EG&G Model 6310 Electrochemical Impedance Analyzer (Princeton Applied Research) run by Model 398 software within a frequency sweep range of 10,000 kHz to 0.01 Hz.

2.5. Cell assembly and testing

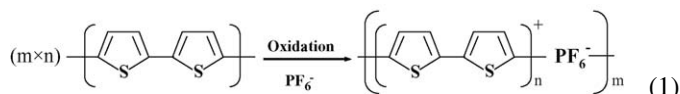
A polypropylene microporous separator was used in the test cells. The separator was sandwiched between the two electrodes. The electrolyte was 1.0 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC), 1:1, v/v, provided by Merck KgaA, Germany. A lithium foil with a thickness of 300 μm and an area of 1.0 cm² was used as the counter electrode. The cells were assembled in an argon-filled glove box (Unilab, Mbraun, USA) with both water and oxygen concentrations less than 5 ppm.

Charge–discharge tests were performed with a battery testing device (Neware, Electronic Co., China) that was interfaced to a computer by means of suitable software. The system was capable of switching between charge and discharge automatically according to pre-set cut-off potentials. The cells were cycled between 2.5 and 4.3 V at a constant current density of 0.1 mA cm⁻².

3. Results and discussion

3.1. Electrochemical polymerization of bithiophene on to stainless-steel mesh

Polybithiophene-hexafluorophosphate (PBiTh/PF₆) could be successfully electrodeposited on to the stainless-steel mesh electrodes either by cyclic voltammetry (CV), a galvanostatic method, or a potentiostatic method. The potentiodynamic growth of PBiTh/PF₆ was performed at 100 mV s⁻¹ over the potential range -0.6 to +1.4 V from a solution containing bithiophene (10 mM)/TBAPF₆ (0.1 M)/DCM. The cyclic voltammogram obtained during PBiTh/PF₆ growth (Fig. 1) shows the expected increase in redox current with increasing number of cycles. This indicative of deposition of conducting electroactive polymer. The oxidation of bithiophene to form a polybithiophene film is according to the following equation:



where n indicates degree of doping [14], and m determines molecular weight.

Based on the first cycle in Fig. 1, the potential chosen for potentiostatic growth of PBiTh/PF₆ was +1.1 V. A typical chronoamperogram of conducting polymer growth is shown in Fig. 2(a). After the initial transient, the current increases steadily as the polymer continues to grow and results in an increase in surface area.

The galvanostatic growth of PBiTh/PF₆ was performed at a constant current density of 0.2 mA cm⁻². The chronopotentiogram (Fig. 2(b)) exhibits an initial transient and then a decreasing potential as expected for the growth of a conducting electroactive polymer. After 10 min, the potential obtained during growth was +0.96 V.

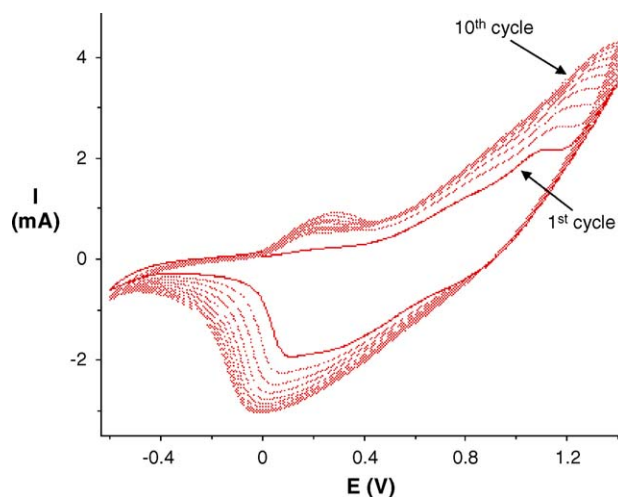


Fig. 1. Potentiodynamic growth of PBiTh/PF₆ film on a stainless-steel mesh from a solution containing bithiophene (10 mM)/TBAPF₆ (0.1 M)/DCM. Range: -0.6 to +1.4 V. Scan rate: 100 mV s⁻¹.

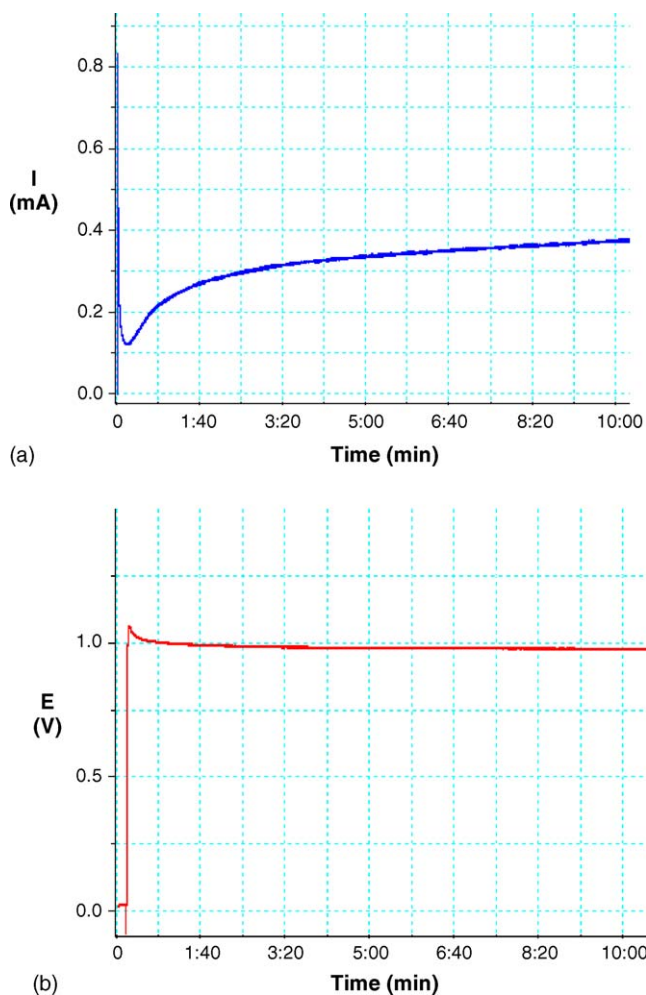


Fig. 2. (a) Chronoamperogram of PBiTh/PF₆ growth on a stainless-steel mesh from a solution containing bithiophene (10 mM)/TBAPF₆ (0.1 M)/DCM by constant potential, +1.1 V; (b) chronopotentiogram of PBiTh/PF₆ growth on a stainless-steel mesh from a solution containing bithiophene (10 mM)/TBAPF₆ (0.1 M)/DCM by constant current density, +0.2 mA cm⁻².

3.2. Morphology of polybithiophene-hexafluorophosphate films

Scanning electron micrographs of polybithiophene-hexafluorophosphate films deposited on stainless-steel mesh are presented shown in Fig. 3. The morphology of PBiTh/PF₆ grown at constant potential (CP) (Fig. 3(a)) is much more porous than that obtained at constant current (CI), see (Fig. 3(b)). This difference will effect their performance in battery testing.

3.3. Electrochemical performance

Typical cyclic voltammograms for cathode of a PBiTh/PF₆ film on stainless-steel mesh in a lithium-polymer battery is shown in Fig. 4. During discharge, the polymer is reduced to its neutral state by releasing the anion A⁻, according to:

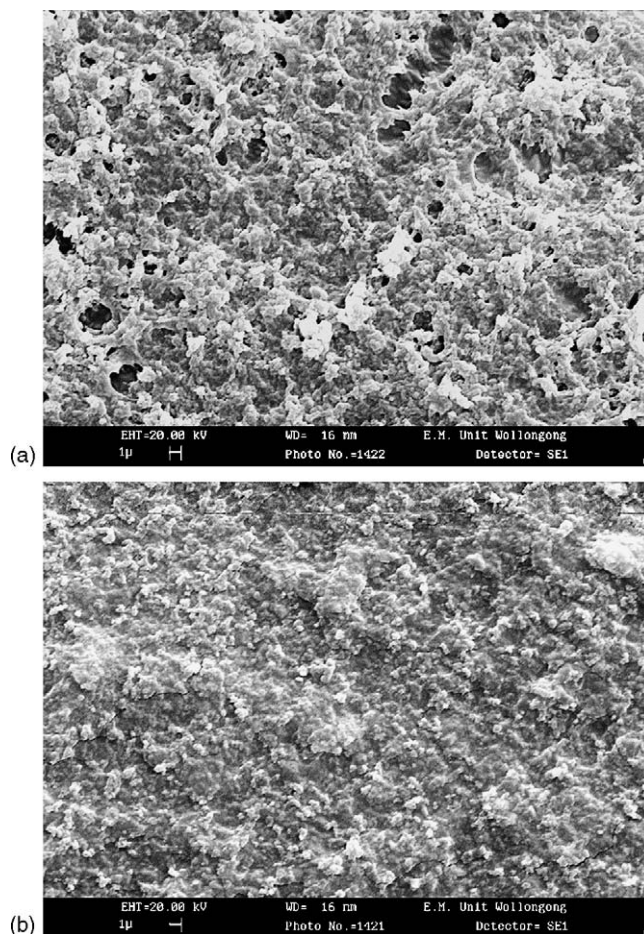
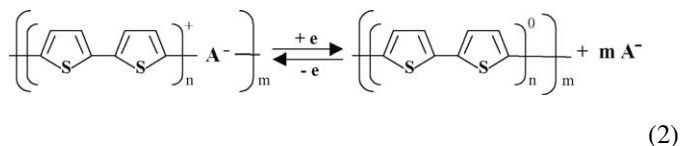


Fig. 3. Scanning electron micrographs of PBiTh/PF₆ films growth under (a) constant potential; (b) constant current.

When charged again, anions migrate back into the polymer. The cyclic voltammety was performed at a scan rate of 20 mV s⁻¹ over the potential range 2.5–4.3 V (versus Li/Li⁺, two-electrode system) in a electrolyte of 1.0 M LiPF₆/EC and DMC (1:1 v/v). A stable redox couple (labeled A and B) is

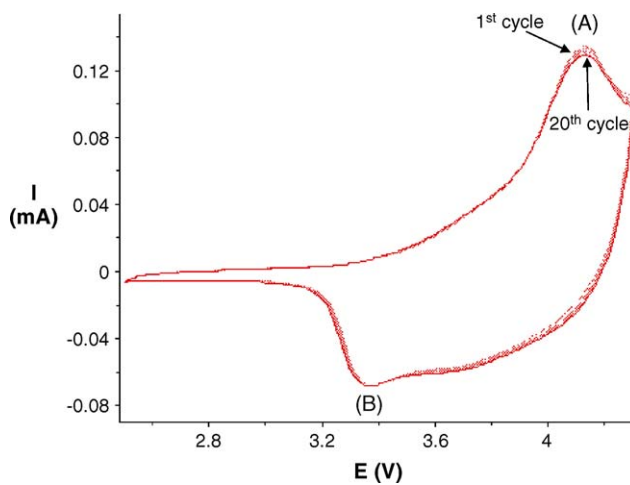


Fig. 4. Cyclic voltammograms of PBiTh/PF₆ coated stainless-steel mesh electrodes in battery test cell with a electrolyte of 1.0 M LiPF₆/EC and DMC (1:1 v/v). Range: +2.5–4.3 V. Scan rate: 20 mV s⁻¹.

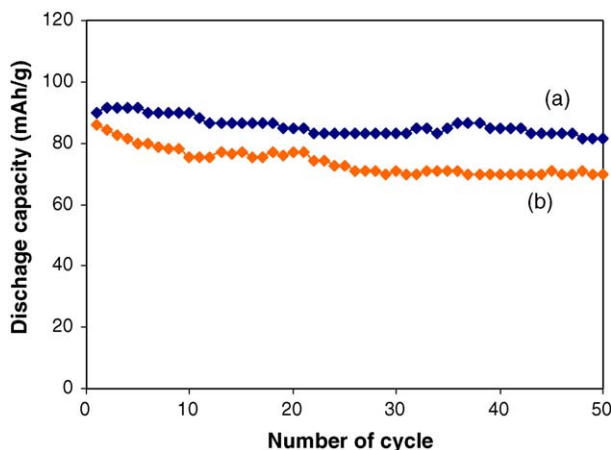


Fig. 5. Discharge capacity vs. cycle number for cathodes of PBiTh/PF₆ coated stainless-steel mesh grown under (a) constant potential; (b) constant current. Discharge current: 0.1 mA cm⁻².

observed and can be assigned to the polybithiophene backbone. After 20 cycles, the peak current has decreased by less than 10%. This demonstrates that polybithiophene sustains a very stable electrochemical activity. No change in colour of the electrolyte was obtained after battery testing. Thus, the mechanical stability of the PBiTh/PF₆ film on stainless-steel mesh is maintained.

The discharge capacities versus the cycle number for cells fabricated with PBiTh/PF₆ films grown by different methods, namely, CP and CI, are shown in Fig. 5. After 50 cycles, the cell with PBiTh/PF₆ grown by CP displays a discharge capacity of 81.67 mAh g⁻¹. The capacity 15% higher than that of the cell with PBiTh/PF₆ grown by CI (69.71 mAh g⁻¹). This is possibly due to the different morphology of the films (Fig. 3). The PBiTh/PF₆ grown by CP with a more porous structure (see Fig. 3(a)) should have a larger surface area, and therefore, a higher reactivity.

Electrochemical impedance spectroscopy (EIS) was performed on stainless-steel mesh electrodes coated with PBiTh/PF₆ films grown by the CP and CI methods. The impedance results obtained from lithium–polymer cells using PBiTh/PF₆ cathode materials are given in Fig. 6. In the high frequencies

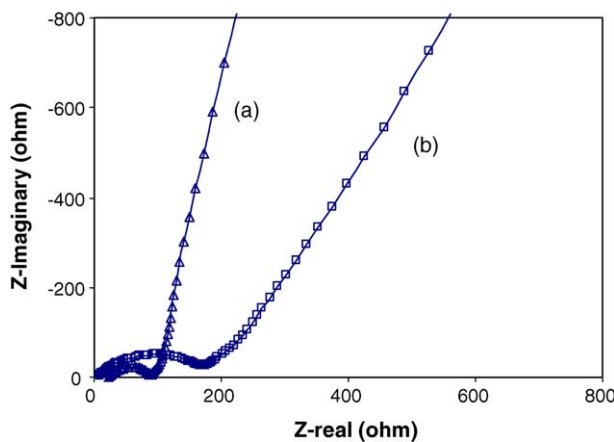


Fig. 6. Impedance plots for PBiTh/PF₆ films on stainless-steel mesh in lithium–polymer battery. Film grown under, (a) constant potential; (b) constant current.

region, both types of PBiTh/PF₆ electrodes display a semicircle loop, which corresponds to the charge-transfer resistance of PBiTh/PF₆ that results from the movement of anions in the film during the charge–discharge process [15]. The charge-transfer resistance of the cell with the PBiTh/PF₆ electrode grown by CP is lower than that of the cell with the PBiTh/PF₆ electrode grown by CI. According to Eq. (2), this strongly suggests that the former electrode sustains a smoother and more stable migration of anions in and out of the polymer film during the charge–discharge process. This is possibly due to the more porous morphology (Fig. 3(a)) of this electrode compared with that for an electrode grown by CI.

4. Conclusions

A rechargeable lithium battery that uses polybithiophene as the active cathode material has been successfully fabricated and evaluated. The best electrochemical performance is obtained from a cell using PBiTh/PF₆ coated stainless-steel mesh (grown by CP) that has a higher stable discharge capacity of 81.67 mAh g⁻¹ over 50 cycles than that given by PPy [8]. This suggests that polybithiophene is a promising cathode material for lithium–polymer rechargeable batteries. The behaviour also shows that the methods used for the polymerization of polybithiophene exist an influence on the electrochemical performance of this material in lithium–polymer cells.

Acknowledgements

Financial support provided by the Australian Research Council (ARC) is gratefully acknowledged.

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