



Electrodeposited polypyrrole (PPy)/para (toluene sulfonic acid) (pTS) free-standing film for lithium secondary battery application

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ABSTRACT

Highly flexible and bendable free-standing polypyrrole-para (toluene sulfonic acid) (PPy-pTS) films were prepared using the electropolymerization method. The films are soft, lightweight, mechanically robust, and highly electrically conductive. The films display a cauliflower-like structure consisting of micron-scale spherical grains, which are related to dopant intercalation in the polymeric chains. The electrochemical behaviour of the free-standing films was examined as cathode against lithium counter electrode. Electrochemical tests demonstrated that the PPy-pTS film with 30 min deposition time exhibited higher discharge capacity (85 mAh g^{-1}) beyond 80 cycles than the PPy-pTS films with 1 h deposition time (76 mAh g^{-1}) and 2 h deposition time (55 mAh g^{-1}) at 0.1 mA cm^{-2} over a potential range of 2.5–4.3 V. The free-standing films can be used as electrode materials to satisfy the new market demand for flexible and bendable polymer batteries.

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1. Introduction

The issue of new solutions for clean and sustainable energy is becoming a critical factor for the future of our society [1,2]. With the population explosion and the depletion of natural resources, people are increasing awareness of environmental protection. Meanwhile, with electronic techniques developing very fast and electronic productions were driven to miniaturization, lower weight, and better performance, great demand for lithium secondary batteries were intensively increasing [3]. Lithium secondary batteries generally have high energy density and are one of the most actively developed batteries with an important application of electro-conductive polymers. The possibility of using conductive polymers as electrode materials for secondary batteries was demonstrated since 1985 [4]. Several conducting polymers such as polypyrrole, polyaniline, and polythiophene have been proved to be promising materials for the electrode of secondary battery because they are stable in air and have good electrochemical properties [5]. Among the conducting polymers, polypyrroles (PPy) have drawn the most attention due to their redox properties, biocompatibility, good electrical conductivity, and chemical stability [7–11]. On the other hand, there has been strong market demand for thin, flexible and bendable electrodes to

make lithium batteries/lithium-polymer batteries that are lighter and more flexible than the existing ones, and thus more capable of satisfying the various design and power needs of soft, portable electronic equipment, such as roll-up displays and wearable devices. Active radio-frequency identification tags and integrated circuit smart cards also require flexible or bendable batteries for durability in everyday use [6].

However, to develop mechanically flexible and bendable lithium batteries, soft and free-standing electrode materials are also required. It has been reported that conducting PPy films can be synthesized by electropolymerization and that the films thus produced can be peeled off from the smooth substrate so that free-standing electrodes are obtained [22]. In order to select a commercially available substrate material for commercial polymer batteries, lightweight and inexpensive stainless steel mesh could be the best choice of substrate but each electrode is formed from a metal substrate that is coated with a mixture of an active material, an electrical conductor, a binder, and a solvent. This kind of electrode is not suitable for flexible or bendable batteries, because a metal substrate is used to hold the active materials. The active material layers will be cracked or peeled off from the substrate when they are bent. So, only the free-standing films can be used as electrode materials to satisfy the new market demand for flexible and bendable batteries. The application of polypyrrole as cathode material for rechargeable batteries has also been reported but has still not been successfully used for commercial batteries because of its poor cycling stability and poor rate capability [8–10,12]. As a common feature, conducting polymers are semiconductors of wide bandgap

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or electrical insulators in their native state. The improvement of the electrical conductivity is typically based on incorporation with an anionic compound, normally called “dopant”, into the polymer matrix. The mechanism of improvement in the electrical conduction in PPy has been attributed to a redox interaction between the conducting polymer and the dopant [13–15]. A variety of anionic dopants have been investigated, including Cl^- [16], ClO_4^- [17], BF_4^- [18], *p*-toluenesulfonate [19], dodecylbenzenesulfonate (DBS) [20], and polystyrene sulfonate (PSS) [21], all of which function to balance the cationic charge of the conductive polymer.

Until now, there have been several reports on the preparation of PPy films doped with *p*-toluenesulfonic acid (*p*TS). Most of these reported works describe the mechanical properties, conductivity, electrochemical relaxation, and ion exchange behaviours of the films [23–32]. Only very few works reported just few electrochemical properties of PPy films doped with *p*TS in an open cell configuration with water based electrolyte for battery/supercapacitor application [33,34]. Unfortunately, none of the reported results shows a wide range of electrochemical characterization of PPy-*p*TS films as cathode using commercial electrolyte in a coin cell configuration within a potential range of 2.5–4.3 V. In this investigation, we report the fabrication and electrochemical characterization of PPy-*p*TS free standing film as cathode for lithium secondary battery. The possibility of directly using free-standing films as battery electrode materials has been examined with a view towards further research on totally flexible and bendable batteries.

2. Experimental

2.1. Preparation of PPy-*p*TS free-standing films

PPy-*p*TS films were electrodeposited using the galvanostatic technique onto a polished stainless steel plate from an electrolyte solution prepared in deionized water with 0.1 mol l^{-1} pyrrole (98%, Sigma–Aldrich) and 0.1 mol l^{-1} para (toluene sulfonic acid) sodium salt (95%, Sigma–Aldrich). Pyrrole was first distilled and kept refrigerated until use. Dissolved oxygen was removed by bubbling the solution with nitrogen for at least 10 min prior to polymerization. A two electrode electrochemical system was used for polymerization at room temperature (27°C), where polished stainless steel plate (washed with acetone in an ultrasonic bath before use) used as a working electrode and stainless steel mesh as a counter electrode. Two parameters (constant current and different deposition time) were considered during the electrodeposition. The current density for galvanostatic deposition was 0.2 mA cm^{-2} , and the deposition time was 30 min, 1.0 h, and 2.0 h, respectively. The resultant films were peeled off from the polished stainless steel plate after the films had been soaked with distilled water for 30 min to remove the residue. Following the electrodeposition, the films were dried in a vacuum oven for 24 h at room temperature. After drying, the prepared flexible free-standing films were cut into $1 \text{ cm} \times 1 \text{ cm}$ pieces and then transferred to an argon filled glove box. The dried films were assembled into coin cells and were tested.

2.2. Instrumental analysis

The resistance measurements (conductivity measurements) of the films were performed on long strips using the American Society for Testing and Materials (ASTM) four-probe technique. A DC current of 0.5 mA was applied across the two electrodes using an EG&G PAR 363 instrument, and the voltage drop across the two inner electrodes was measured using a HP multimeter (model 34401A). The morphologies of the films were obtained from field emission scanning electron microscopy (FE-SEM; JEOL JSM-7500FA equipped

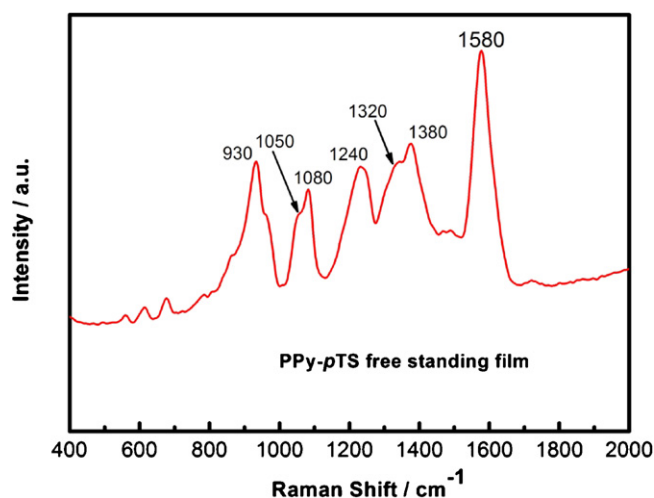


Fig. 1. Raman spectrum of free-standing PPy-*p*TS film.

with energy dispersive X-ray spectroscopy (EDS) and an EDS mapping system). Raman spectroscopy was carried out to monitor the variations using a JOBIN YVON HR800 Confocal Raman system with 632.8 nm diode laser excitation on a 300 lines/mm grating at room temperature.

2.3. Electrochemical measurements

The electrochemical measurements were carried out using coin cells. CR 2032 coin-type cells were assembled in an Ar-filled glove box (Mbraun, Unilab, Germany) by stacking a coin shaped porous polypropylene separator containing liquid electrolyte between the PPy-*p*TS free-standing electrodes with a area of 1 cm^2 and a lithium foil counter electrode with a thickness of $300 \mu\text{m}$ and area of 0.78 cm^2 . The electrolyte used was 1 M LiPF_6 in a 50:50 (v/v) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC), provided by Merck KGaA, Germany. Charge–discharge tests were carried out by using a battery testing device (Neware Electronic Co., China) interfaced to a computer with software. The system is capable of switching between charge and discharge automatically according to the pre-set cut-off potentials. The cells were cycled between potential of 2.5 and 4.3 V with a constant current of 0.1 mA cm^{-2} . Electrochemical impedance spectroscopy (EIS) was performed using a CHI 660C electrochemistry workstation. The AC amplitude was 5 mV, and the frequency range applied was 100 kHz–0.01 Hz.

3. Results and discussion

Raman spectra obtained for the PPy-*p*TS film (Fig. 1) also matched those reported previously for typical PPy [35–37]. The strong band located at approximately 1580 cm^{-1} represents the C=C backbone stretching of PPy. The double peaks at about 1050 and 1080 cm^{-1} are assigned to a C–H in-plane deformation. The other double peaks at approximately 1320 cm^{-1} and 1380 cm^{-1} are attributed to the ring-stretching mode of PPy. The bands at 930 cm^{-1} and 1240 cm^{-1} are attributed to the C–H out-of-plane bending of oxidized PPy and C–H or N–H in-plane bending, respectively. As reported in the literature [38,39], the C=C peak is related to the conjugation length of PPy and the doping level.

Polymerization of pyrrole (Py) produces the highly conductive and oxidized (doped) form of polypyrrole, in which some electrons are removed from a delocalised π -system. The electro-neutrality of the oxidized polymer is retained by the incorporation of an

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