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Synthesis of a novel ferrocene-contained polypyrrole derivative and its performance as a cathode material for Li-ion batteries☆

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ABSTRACT

A novel ferrocene-contained pyrrole, 4-(1H-pyrrol-1-yl) phenyl ferrocenecarboxylate (FcPy) was synthesized by esterification of 4-(1H-pyrrol-1-yl) phenol (PLPY) and ferrocenecarboxylic acid. Then the homopolymer of FcPy (PFcPy), copolymer of FcPy and pyrrole (P(FcPy-co-Py)), polypyrrole (PPy) were prepared by chemical oxidative polymerization. And the structure, morphology, electrochemical properties of prepared polymers were characterized by fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), cyclic voltammograms (CV) and electrochemical impedance spectra (EIS), respectively. Also, the charge/discharge properties of the prepared polymers were studied by galvanostatic charge–discharge testing. The results demonstrated that the introduction of ferrocene to polypyrrole obviously improved the specific capacity of PPy cathode and gave a well-defined plateau at the potential rang of about 3.5 V. Under our experimental conditions, the discharge capacity of undoped PPy-based electrodes only presented 16.5 mAh g^{-1} at 20 mA g^{-1} between 2.5 and 4.2 V, while PFcPy-based electrodes exhibited an initial discharge capacity of up to 43.2 mAh g^{-1}. Specially, the P(FcPy-co-Py)-based electrodes even showed a discharge capacity of 68.1 mAh g^{-1} and the improved discharge platform, which were ascribed to the resonance doping effect of pendant group, the advanced electrochemical nature of ferrocene moiety and the loose morphology of copolymer.

1. Introduction

In recent years, one of the most challenges in modern society is to find a suitable power that will satisfy our growing portable power requirements with the developing of electronic products. Li-ion batteries, as demonstrated by their wide applications in portable electronic devices, have been considered to be the most promising technology in the future [1–3]. Whereas, the wide use of this technology is mainly restricted by the positive electrode, which usually shows a much lower capacity than that of the negative one. Therefore, many attempts have been paid to the development of a promising positive electrode with high capacity and high stability. Currently, many effects mainly focus on the inorganic transition-metal-oxide-based materials (such as $LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$ and V_2O_5, etc.), which have a series of disadvantages, such as limited mineral resources and waste treatment process. In addition, the high energy demand and CO_2 emissions during the producing process also limit their large scale applications for upcoming electric vehicles and renewable power stations [4–6]. Therefore, the novel cathode materials are still highly desired for the development of advanced Li-ion batteries. To address this issue, one of the most attractive approaches is the utilization of organic cathode materials [7–9] because of their easy preparation and high energy density, as well as a possibility for the design of any size and shape of electrode films for flexible Li-ion batteries, although they have some known problems, such as relatively poor performances in capacity and stability, and others. So far, several types of organic positive-electrode materials have been proposed, mainly including of electroactive conducting polymers [7,10], organosulfur polymers [11], nitroxide radical tetramethylpiperidine-N-oxyl (TEMPO)-based polymers [12,13], pendant-type polymer based on ferrocene and carbazole [14,15], aromatic carbonyl derivatives and quinine-based materials [16], etc.

Among them, conducting polymers seem to be a most probable candidate because of their high electronic conductivity and reversible redox-active chemistry. In particular, p-doped polymers such as polyaniline (PAn) [17], polypyrrole (PPy) [18,19], polythiophene (PTh) [20,21], and their derivatives are frequently reported as organic cathode materials for rechargeable batteries. These polymers can be charged and discharged by a redox reaction, which

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companies an inserted/de-inserted process of both lithium ions and counter anions in the electrolyte. Among the conducting polymers, PPy is one of the most popular for use as a cathode, because of its environmental stability, high specific energy (ranging from 80 to 390 Wh kg^{-1}) [7] and theoretical capacity (~400 mAh g^{-1}). However, the electrodes so far synthesized have several problems relating to the generally low realizable capacity (due to the low doping degree) and the sloping charge–discharge curves (due to the nature of doping process), which have limited the practical applications of PPy in energy storage devices.

Ferrocene as an organometallic compound has been extensively investigated as a standard electrode in the redox potential measurement because of its air stability, excellent electrochemical response, redox property, and so on. [22–25] Recently,[14] it has been reported that polymers carrying ferrocene moieties such as poly(vinlferrocene), poly(ethynylferrocene) and poly(ferrocene) have been applied as cathode-active materials in organic lithium ion batteries, which exhibits promising battery properties such as high power density and the stable voltage plateaus (~3.4 V). Moreover, Park's group recently anchored ferrocene groups to the PPy backbone, and the prepared PPy-based copolymer attaching the redox couples demonstrated a flat charge–discharge curve over all capacity range and an additional capacity comparing to that of PPy. [10] The obtained ferrocene modified PPy copolymer is mainly utilized as the coatings to study its effects on improving $LiFePO_4$ performances. However, the detail investigation on the influence of ferrocene on the electrochemical properties of PPy has not been further explored just now.

In this work, a novel ferrocene-containing pyrrole was synthesized, and the homopolymer of FcPy (PFcPy), copolymer of FcPy and pyrrole P(FcPy-co-Py), polypryyole (PPy) were prepared by chemical oxidation polymerization. And the electrochemical properties of above three polymers as cathode materials of lithium ion battery were systematically investigated by lithium ion half-cell method, comparatively. Also, the effects of ferrocene moiety on the performances of the PPy-based cell were investigated. Moreover, the possible mechanism for the improvement of the electrochemical properties was further discussed. In order to eliminate the effects of the uncertainly doping level on the research, the polymers in the study were adopted in the undoped state. Thanks to the introduction of ferrocene-based pendants in PPy backbone, we found that the (PFcPy)- and/or P(FcPy-co-Py)-based electrode remarkably improved discharge voltage plateaus and charge–discharge performance compared to the pristine PPy electrode and were promising as advanced cathode material.

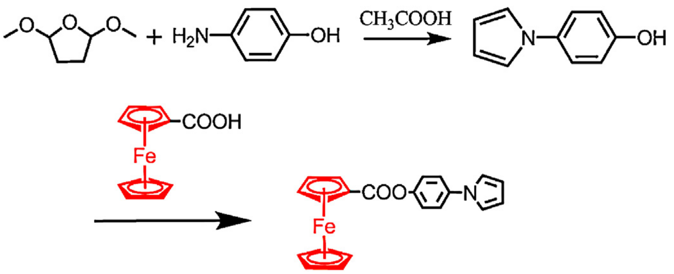
2. Experimental

2.1. Materials

2,5-Dimethoxytetrahydrofuran (98%), 4-aminophenol (98%), pyrrole (99%) were purchased from Aladdin-Reagent Co. Pyrrole was purified by distillation before use. Ferrocene carboxylic acid (99%) was purchased from Energy Chemical Reagent Co. All other reagents were received as analytical grade and used without further purification.

2.2. Synthesis of FcPy

The synthesis of the monomer (FcPy) is shown in Scheme 1.



Scheme 1. The synthesis route to FcPy.

2.2.1. Synthesis of 4-(1H-pyrrol-1-yl) phenol

2,5-Dimethoxytetrahydrofuran (6.46 ml, 0.05 mol) and 4-aminophenol (5.4 g, 0.05 mol) were dissolved in a mixture of 20 ml deionized water and 40 ml glacial acetic acid, and heated reflux (70 °C) for 1 h until the solution turned to jacinth. The reaction mixture was then cooled and extracted with CH_2Cl_2, and the organic fraction was washed with saturated brine for three times. The organic phase was separated, dried, and evaporated to dryness. Flash chromatography of the residue (silica gel, petrol ether/ethyl acetate 20:1) afforded the title compound (3.47 g, 52% yield) as a white powder. ^1H NMR ($CDCl_3$, 400 MHz) d/ppm: 4.80 (s, 1H); 7.01 (t, 2H); 6.35 (t, 2H); 6.90 (d, 2H); 7.28 (d, 2H).

2.2.2. Synthesis of FcPy

Ferrocene carboxylic acid (1.518 g) and 4-(1H-pyrrol-1-yl)phenol (0.955 g) were dissolved in the mixture of 40 ml dichlormethane and 25 ml DMF in the pre-dried three-necked flask, then 0.15 g 4-dimethylaminopyridine was added as acylating catalyst and 1.35 g N,N′-dicyclohexylcarbodiimide as dehydrating agent, and stirring for 24 h at room temperature. The reaction mixture was then separated by vacuum filtration. The filtrate was washed with saturated brine for three times. Organic phase was dried over sodium sulfate. The ester was purified by column chromatography using silica gel and petroleum ether/ethyl acetate afforded the title compound as golden flakes like crystals. ^1H NMR ($CDCl_3$, 400 MHz) d/ppm: 4.99 (t, 2H), 4.54 (t, 2H), 4.33 (s, 5H), 6.38 (d, 2H), 7.09 (d, 2H), 7.26 (d, 2H), 7.45 (d, 2H).

2.3. Chemical polymerization of PPy, PFcPy and P(FcPy-co-Py)

All of PPy, P(FcPy-co-Py) and PFcPy were prepared by the same methods. Py, FcPy or Py/FcPy monomers (molar ratio of FcPy/Py = 1:5) was dissolved in methanol. $FeCl_3$ $6H_2O$ in methanol ($FeCl_3$ $6H_2O$/[FcPy + Py] molar ratio = 2.5:1) were then slowly added with dropwise. The reaction was conducted under nitrogen atmosphere at room temperature for 24 h. Afterwards, the precipitates were filtered and washed with methanol and deionized water alternately till the filtrate was clear. The polymers were dried under vacuum for 24 h at 60 °C.

2.4. Characterization and electrochemical measurements

FT-IR spectra were carried out on a Nicolet 6700 spectrometer (Thermo Fisher Nicolet, USA) with KBr pellets. UV–vis spectra were recorded on a Varian Cary 100 UV–vis spectrophotometer (Varian, USA). ^1H NMR spectra of the compounds were recorded on a Bruker AVANCE III 500 MHz spectrometer (Bruker, Switzer-land) using $CDCl_3$ Scanning electron microscopy (SEM) measurements were taken using a Hitachi S-4800 scanning electron microscope (Hitachi, Japan).

For cathode characterization, CR2032 coin-type cell was used and assembled in an argon-filled glove box. The cathode electrodes were prepared by coating a mixture containing 50% as prepared polymers, 40% acetylene black, 10% PVDF binder on circular Al current collector foils, followed by dried at 60 °C for 10 h. After that, the cells were assembled with lithium foil as the anode, the prepared electrodes as cathode and 1 M $LiPF_6$ dissolved in ethylene carbonate