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Facile electrochemical polymerization of 2-(thiophen-2-yl)furan and the enhanced capacitance properties of its polymer in acetonitrile electrolyte containing boron trifluoride diethyl etherate

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ABSTRACT

In this study, a new simple hybrid poly(2-(thiophen-2-yl)furan) (PTFu) was easily electrodeposited by direct anodic oxidation of 2-(thiophen-2-yl)furan in acetonitrile solution containing 0.1 M lithium perchlorate ($LiClO_4$). The oxidation onset potential of 2-(thiophen-2-yl)furan monomer in this medium was measured to be 0.90 V, which was lower than those of thiophene (1.47 V) and furan (1.28 V). The structure and morphology of PTFu were characterized by Ultraviolet–visible spectroscopy, Fourier transform infrared spectroscopy, scanning electron microscopy, and thermal analysis. The electrochemical capacitance properties of PTFu electrode in three electrolytes were also investigated by cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscope techniques. The electrochemical results showed that the specific capacitance of PTFu electrode was enhanced to 392.0 $F\,g^{-1}$ from 249.4 $F\,g^{-1}$ at 5 $A\,g^{-1}$ and the cycling stability was also enhanced to 67.0% retention from 25.5% retention after 500 cycles when the equivalent boron trifluoride diethyl etherate (BFEE) was added into the acetonitrile electrolyte. Furthermore, the PTFu electrode in ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($BmimPF_6$) showed a lower specific capacitance value (209.4 $F\,g^{-1}$ at 5 $A\,g^{-1}$) and an improved stability (67.6% retention after 600 cycles). These results indicated that the conducting polymers based on furan should be a promising electrode material for supercapacitor applications when the electrolyte based-BFEE is used.

1. Introduction

Among conducting polymers (CPs) such as polypyrrole (PPy), polyaniline (PANI) and polythiophene (PTh), PTh is one of the most promising electrode materials owing to its high conductivity, environmental stability and its widely potential applications in batteries [1,2], electrochromic displays [3–5] and thermoelectrics [6–8]. Currently, many electrode materials based on PTh such as pristine PTh [9], PTh-carbon nanotube composites [10], PTh-graphene nanocomposites [11] have been studied in the aspect of supercapacitors application. The above reported materials had specific capacitance of about 100∼180 $F\,g^{-1}$ [9–11]. For the synthesis of PTh, the electrochemical polymerization was one of the most useful approaches because of its several advantages, such as one-step deposition of CPs film, catalyst free, ease of characterization, *etc*. However, the oxidation onset potential of thiophene monomer is generally higher than 1.6 V in the neutral solvent, and the electrochemical preparation of PTh from neutral solvent often results in poor materials due to the presence of the overoxidation at such high potential. In order to decrease the oxidation onset potential of thiophene, some strategies have been developed, firstly, introducing substituent groups into thiophene ring such as 3-methylthiophene and 3,4-ethylenedioxythiophene, secondly, using boron trifluoride diethyl etherate or ionic liquids as solvent. Additionally, the oxidation onset potential also lowered via extension of conjugation [12–16]. For example, Rasch *etal* reported that the polymerization potential of thiophene, bithiophene and terthiophene gradually decreased with increasing the conjugated chain of thiophene, and the charge capacity of the resulting polymers increased in the order of PTh, polybithiophene and polyterthiophene [17]. Therefore, these CPs obtained by using long conjugated chain oligomers as starting reactant possibly show the preferable properties.

Most recently, furan was found to have some unique properties even better than thiophene, namely, higher fluorescence, smaller overlap integrals, higher HOMO, lower polarizability, greater rigidity, and improved solubility [18–23]. The furan-based

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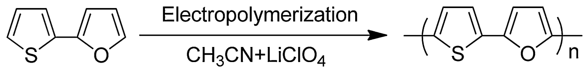
materials were also found to have potential applications in organic electronic devices such as field-effect transistor and photovoltaic applications [24,25]. However, polyfuran (PFu) prepared from the electrochemical polymerization of furan monomer showed low conductivities, poor mechanical properties and ill-defined electrochemical behavior, which mainly resulted from the high oxidation potential of furan in the neutral solvent system [26–29], for example, the oxidation onset potential of furan was above 2.1 V vs SCE in acetonitrile using sodium perchlorate ($NaClO_4$) as the electrolyte [27,30]. Such high oxidation potential of furan extremely limited the study on the electrosynthesis, properties and application of PFu and its derivatives.

However, in view of the outstanding characteristics of furan, it is very necessary to prepare and research novel furan-based materials. Recently, Önal *etal.* reported the low band gaps multichromic polymers based on furan and benzochalcogenodiazole, namely, poly(4,7-di(furan-2-yl) benzo[*c*][1,2,5]selenadiazole) and poly(4,7-di(furan-2-yl) benzo[*c*][1,2,5]thiadiazole), which were electrochemically prepared at lower oxidation potentials [31]. Skabara *etal.* introduced the furan unit with a dithiin ring into thiophene backbone, *viz.* 2,3-bis(methylthio)-5,7-di(thiophen-2-yl)-[1,4]dithiino[2,3-*c*]furan, as-formed polymer exhibited efficient charge delocalisation and better electrochromic properties compared to polythiophene analogues [19]. In our previous work, we studied the electrochemical polymerization of furan, bifuran and trifuran in dichloromethane (CH_2Cl_2)–tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6) (0.1 mol L^{-1}), respectively [23]. It was found that, with the conjugated chain length of monomers increasing, the oxidation onset potential of monomers decreased from 1.25 V to 0.7 V and as-formed polymers showed better electrochemical activity, at the same time, the trifuran was beneficial to prepare the free-standing PFu films with improved optoelectronic properties. Looking back and ahead, it should be proposed that the combination of furan and thiophene will be an effective way to develop a simple structural furan-based material. The proposal is to be feasible because the combination of furan and thiophene increases their conjugated chain length, which may greatly lower the oxidation onset potential of furan and thiophene. To the best our knowledge, there is no report on the investigations of furan-based materials in supercapacitor.

In this paper, 2-(thiophen-2-yl)furan (TFu) was easily electropolymerized into poly(2-(thiophen-2-yl)furan) (PTFu) on platinum electrode in acetonitrile solution containing 0.1 M lithium perchlorate ($LiClO_4$) (Scheme 1). The structural characterization, morphology, and thermal stability of as-formed PTFu film were investigated in detail. The capacitive performances of PTFu in three different electrolytes were also studied by cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy techniques. More interestingly, it was found that PTFu electrode showed fairly high specific capacitance and stability when the equivalent boron trifluoride diethyl etherate was added into the acetonitrile electrolyte.



Scheme 1. Chemical structure and electrochemical polymerization of TFu.

2. Experimental

2.1. Chemicals

2-(thiophen-2-yl) furan (TFu) and anhydrous lithium perchlorate ($LiClO_4$) were purchased from the Sigma–Aldrich (USA). Acetonitrile (CH_3CN, > 99%, Beijing East Longshun Chemical Plant) was purified by distillation with calcium hydride under a nitrogen atmosphere before use. Boron trifluoride diethyl etherate (BFEE, Beijing Changyang Chemical Plant, China) was distilled and stored at $-20\,^{\circ}C$ before use. 1-Butyl-3-methylimidazolium hexafluorophosphate ($BmimPF_6$) (> 99%) was purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences (Lanzhou, China) and used as received.

2.2. Preparation of PTFu electrode

Generally, high quality polymer films can be prepared by the potentiostatic method, such as polythiophenes [32], poly (3,4-ethylenedioxythiophene) [33], polyfuran [23,34] and its comonomers [35], etc. Therefore, in order to characterize the properties of polymer film, the potentiostatic method was used to prepare polymer film. In this work, the PTFu electrode was prepared by potentiostatic method at suitable electrode potential (1.05 V) on Pt substrate in a one-compartment cell using a CHI 660B potentiostat/galvanostat (Shanghai Chenhua Instrumental Co., Ltd. China). The electrolyte solution was CH_3CN containing 30 mM monomer and 0.1 M $LiClO_4$. All the electrochemistry experiments were performed in a conventional three electrode cell at room temperature. An Ag/AgCl electrode (ferrocene, $E_{1/2}$= 0.07 V) was used as the reference electrode, and two platinum wires (1.0 mm diameter) were used as the work electrode and the counter electrode, respectively. After polymerization, the working electrode was taken out from the electrolyte solution, washed thoroughly with CH_3CN to remove any residue, and then dried under the air for further characterization.

The mass of polymer film (m) was calculated from the total charge passed through the cell during the film growth process, according to Eq. (1) [36]:

$$m = \frac{(\eta Q_{\mathrm{dep1}})(M_1)}{FZ_1} \tag{1}$$

Here, m is calculated by using total deposition charge (Q_{dep1}) (the total charge passed through the cell during the polymer film growth process), assuming a 100% current efficiency (η). M_1 is the molecular weight of TFu, F is the Faraday constant (96,485 C/mol). Z_1 is the number of electrons transferred per monomer attached to the polymer, in which $Z_1 = 2 + f$ [37]. The partial charge f is called the doping level, the calculated f was about 0.25 for PTFu electrode in the experiments, assuming a 100% current efficiency (η), according to Eq. (2) [38]:

$$f = \frac{2Q_o}{Q_d - Q_o} \tag{2}$$

Where Q_d is the total charge used for PTFu deposition, and Q_o is the total charge of oxidized species in the polymer film.

2.3. Physical characterization

The surface morphologies of the resultant polymer were investigated by means of a JEOL JSM-6700F scanning electron microscope. Infrared spectra were recorded using a Nicolet 510P FT-IR spectrometer with KBr pellets over the range from 400 cm^{-1} to 4000 cm^{-1}. Ultraviolet–visible spectroscopy (UV–vis) was measured on a UV–vis spectrophotometer (Agilent 8453). The thermogravimetric analysis (TGA) was performed with a thermal analyzer of NETZSCH TG209 under a nitrogen stream in the temperature range of 295–1173 K with a heating rate of 10 K/min.