

Short Communication

Supercapacitor Electrodes Based on Furan-EDOT Copolymers via Electropolymerization

Shijie Zhen, Xiumei Ma, Baoyang Lu, Shouli Ming, Kaiwen Lin, Li Zhao, Jingkun Xu*, Weiqiang Zhou*

Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang 330013, China

*E-mail: xujingkun@tsinghua.org.cn; zhouweiqiang911@126.com

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A series of furan-EDOT copolymer films, namely, P(Fu-EDOT), P(Fu-EDOT-Fu) and P(EDOT-Fu-EDOT), were electrochemically synthesized from their corresponding monomers and evaluated as active electrode materials for supercapacitor applications by galvanostatic charge–discharge method. The specific capacitance of these copolymers was calculated to be 65, 46 and 75 F g⁻¹ at a current density of 1 A g⁻¹, respectively. Besides, their energy density were also investigated. Among them, P(EDOT-Fu-EDOT) exhibited higher specific capacitance and energy density (15 Wh kg⁻¹ at a power density of 0.6 KW kg⁻¹) than P(EDOT-Fu) and P(Fu-EDOT-Fu), and also showed a large power range while maintaining a relatively high energy density. These favorable performances make P(EDOT-Fu-EDOT) a promising candidate as electrode material for supercapacitors compared with P(Fu-EDOT-Fu) and P(EDOT-Fu).

Keywords: Supercapacitors, PEDOT, Polyfuran, Electropolymerization, Specific capacitance

1. INTRODUCTION

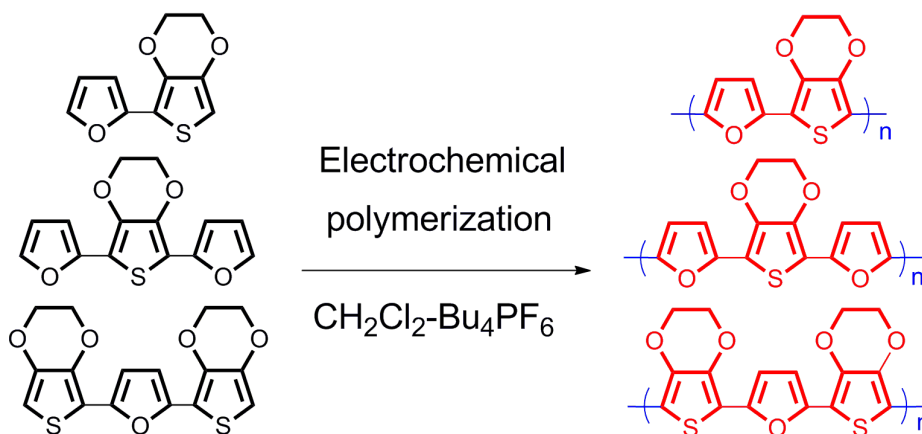
Owing to the tremendous increase in energy consumption in modern society, the development of sustainable and renewable energy sources is urgently required [1,2]. Supercapacitors, as a kind of efficient energy storage devices, which fill the gap between batteries and conventional capacitors due to their satisfactory performance of higher power density and better cycling lifespan over batteries and higher energy density than conventional capacitors, have attracted increasing attention in recent years [3-5]. Currently, the mostly studied electrode materials for supercapacitor mainly are carbon materials, metal oxides, and conducting polymers. Carbon materials as supercapacitor electrodes are attractive candidates because of their high electronic conductivity and large specific surface area [6], but with limited capacitance values (15-200 F g⁻¹) [7]. Among available metal oxides, RuO₂ shows the best

performance [8]. But its high cost and toxic nature significantly limit commercial application [9]. Alternative the cheaper metal oxides NiO, cannot be used at potential windows above 0.6 V; furthermore, most of them are poorly conductive [10]. Conducting polymers (CPs), such as polypyrrole (PPy), polyaniline (PANI) and polythiophene (PTh) and their derivatives [11], have been considered as promising candidates because of their high theoretical specific capacitances, low cost, facile synthesis, fast charge/discharge electron-transfer kinetics, and high conductivity in the doped state [12]. However, only a limited number of studies investigated their close analogue, furan and its-based materials, which has been found potentially useful for device applications most recently [13-22]. The reasons accounting for this phenomenon are probably the susceptibility of the furan on the side reactions during the polymerization and low stability of the resulting polymers [23-26].

On the other hand, recent studies showed that furan containing polymers have some priorities over thiophene based ones for polymer organic electronics in advanced technological applications. For instance, the field-effect mobilities of furan derivatives are very similar to the thiophene based one, and this property together with natural feed-stock and higher open circuit voltage when compared its five-membered analogues make furan based polymers outstanding candidates for organic electronics [27]. Furthermore, furan-based heterocycles were introduced as peripheral substituents on one of the highest performing small molecules for photovoltaics [16]. More importantly, furan monomer and its derivatives can be obtained from biomass and biodegradable relative to traditional organic electronic materials and are considered as “green” electronic materials [27]. However, the supercapacitor performances of furan-based conducting polymers have not been reported so far, which would probably exhibit some interesting findings due to their unique optoelectronic properties.

Poly(3,4-ethylenedioxythiophene) (PEDOT) is considered to be a prospective electrode material due to its high conductivity, fast charge/discharge ability, wide potential window, and good environmental stability [28,29]. Recently, Li et al. reported that the introduction of PEDOT species on the graphene sheets induced the formation of ordered MnO₂ nanowires because of the matched chemical bond of PEDOT and MnO₂ species [30]. Its monomer, 3,4-ethylenedioxythiophene (EDOT), has been employed as a building block in the design of conjugated systems, which incorporate unique properties such as capacitance properties [31]. Although the electrochemical properties and quality of obtained furan-EDOT copolymer films could be improved via incorporating the EDOT unit into polyfuran chain length [32], few studies have attempted to characterize the capacitance properties of furan-EDOT copolymer films.

We herein systematically investigated the supercapacitor performances of electrosynthesized furan-EDOT copolymer films from different furan-EDOT precursors, namely, from 5-(furan-2-yl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxin (Fu-EDOT), 5,7-di(furan-2-yl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxin (Fu-EDOT-Fu), and 2,5-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)furan (EDOT-Fu-EDOT), as shown in Scheme 1.



Scheme 1. Synthetic routes of furan-EDOT polymer films.

2. EXPERIMENTAL SECTION

2.1 Chemicals

The furan-EDOT monomers, 5-(furan-2-yl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxin (Fu-EDOT), 5,7-di(furan-2-yl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxin (Fu-EDOT-Fu), and 2,5-bis(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)furan (EDOT-Fu-EDOT), were synthesized perviously by Stille coupling reaction, a convenient method for the formation of aromatic C-C bond, combining EDOT unit and furan unit to give the target compounds in satisfactory yields as we reported previously [32]. Dichloromethane (analytical grade; Beijing East Longshun Chemical Plant) was purified by distillation with calcium hydride under a nitrogen atmosphere before use. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6 , 99%; Energy Chemical) was dried under vacuum at 60 °C for 24 h before use. Other chemicals and reagents (analytical grade, >98%) were all purchased commercially from Beijing East Longshun Chemical Plant (Beijing, China) and were used directly without any further treatment.

2.2 Electrosynthesis and electrochemical tests

All the electrochemical experiments and polymerization of the monomers were performed in a one-compartment cell with the use of CHI 660B potentiostat/galvanostat (Shanghai Chenhua Instrumental Co., Ltd., China). For electrochemical tests, the working and counter electrodes were both Pt wires with a diameter of 1 mm, respectively. They were placed 5 mm apart during the examinations. Prior to each experiment, these electrodes mentioned above were carefully polished with 1500 mesh abrasive paper, cleaned successively with water and acetone, and then dried in air. An Ag/AgCl electrode directly immersed in the solution served as the reference electrode, and it revealed sufficient stability during the experiments. All the solutions were deaerated by a dry nitrogen stream and maintained under a slight overpressure through all the experiments to avoid the effect of oxygen.

2.3 Preparation of furan-EDOT polymer films modified electrode

The polymer films were grown potentiostatically at the optimized potential in $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ (0.1 mol L^{-1}) and its thickness was controlled by the total charge passed through the cell, which was read directly from current-time (I-t) curves by computer. After polymerization, the polymer films were washed repeatedly with anhydrous CH_2Cl_2 to remove the electrolyte, monomers, and oligomers.

The mass of polymer film (W_{polymer}) is calculated from the total charge passed through the cell during the film growth process, according to Eq. (1) [33,34]:

$$W_p = \frac{(\eta Q_{\text{dep}})(M)}{FZ} \quad (1)$$

Here, W_{polymer} is calculated by using the total charge (Q_{dep1}) passed through the cell during the polymer film growth process, assuming a 100% current efficiency. M_1 is the molecular weight of furan-EDOT monomers. F is the Faraday constant (96485 C/mol). Z_1 is the number of electrons transferred per monomer attached to the polymer, in which $Z_1 = 2 + f$ [35-37]. The partial charge f is called the doping level, the calculated f is about 0.3, assuming a 100% current efficiency (η), according to eq. (2) [36,38]:

$$f = \frac{2Q_o}{Q_d - Q_o} \quad (2)$$

Where Q_d is the total charge used for copolymer deposition, and Q_o is the total charge of oxidized species in copolymer films.

2.4 Galvanostatic charge-discharge tests

Galvanostatic charge-discharge tests were performed in a one-compartment cell with the use of CHI 660B potentiostat/galvanostat (Shanghai Chenhua Instrumental Co., Ltd., China). The working electrode was furan-EDOT copolymer modified Pt wire with a diameter of 1 mm and the counter electrode was Pt wire. An Ag/AgCl electrode directly immersed in the solution served as the reference electrode, and it revealed sufficient stability during the experiments. The charge and discharge current were ranged from 0.1 to 10 μA with cut off voltage of -0.3-1.1 V for furan-EDOT copolymer capacitor.

3. RESULTS AND DISCUSSION

3.1 Capacitance properties of furan-EDOT copolymers electrode

Galvanostatic charge-discharge tests were carried out to evaluate the capacitance of furan-EDOT copolymers modified electrode at a series of current densities using a potential window of -0.3-1.1 V vs. Ag/AgCl, as shown in Fig. 1. Herein, the specific capacitance (C , F g^{-1}) obtained from galvanostatic charge/discharge method can be calculated according to Eq. (3) [39]

$$C = \frac{I \times t}{m \times V} \quad (3)$$

where C is specific capacitance (F g^{-1}), I and t are the discharge current and time, respectively, V is the potential range, and m is the mass of electrode materials.

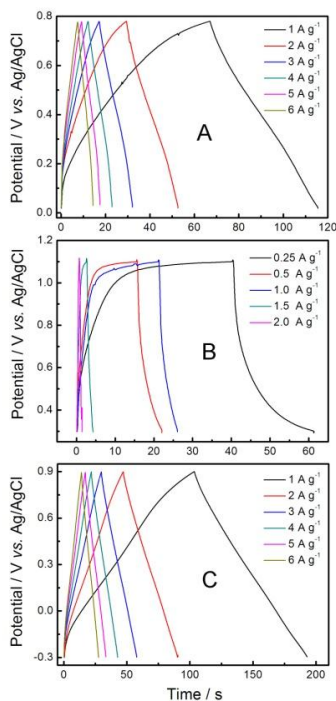


Figure 1. Galvanostatic charge/discharge curves of P(EDOT-Fu) (A), P(Fu-EDOT-Fu) (B) and P(EDOT-Fu-EDOT) (C) films in monomer-free $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ (0.1 mol L^{-1}) at different current density.

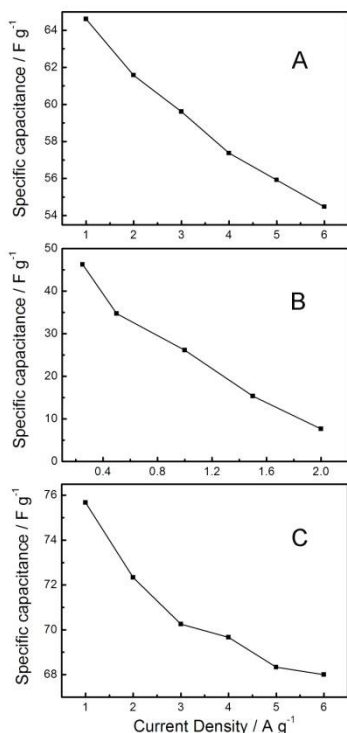


Figure 2. Specific capacitance as a function of current density of P(EDOT-Fu) (A), P(Fu-EDOT-Fu) (B) and P(EDOT-Fu-EDOT) (C) films in monomer-free $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ (0.1 mol L^{-1}).

Fig. 2 reveals the specific capacitance of furan-EDOT copolymer films at different current densities calculated by equation upward, respectively. As can be seen in Fig. 2, the specific capacitance

of P(EDOT-Fu-EDOT) was 75 F g^{-1} at a current density of 1 A g^{-1} , which was higher than those of P(EDOT-Fu) (65 F g^{-1}) and P(Fu-EDOT-Fu) (46 F g^{-1}). From our previous report [32], the onset oxidation potential of EDOT-Fu-EDOT was lower than the other two. And as we known, low oxidation potentials should provide considerably milder polymerization conditions and yield higher quality polymer films. The difference in the specific capacitance of the three furan-EDOT copolymers might attributed to the lower potential in preparing copolymer films and the electron-donating ethylenedioxy group in EDOT unit [40,41].

For further investigation of the electrochemical performance of furan-EDOT copolymers modified electrode in the electrolyte, the power density (P) and energy density (E) values can be calculated from the following Eq. (4) and Eq. (5) [40]:

$$E = \frac{1}{2} CV^2 \quad (4)$$

$$P = \frac{E}{\Delta t} \quad (5)$$

Where C is the specific capacitance calculated according to Eq. (5), V is potential window (V), P and E are power density (KW kg^{-1}) and energy density (Wh kg^{-1}) of the electrode, respectively, and Δt is the discharge time for the potential.

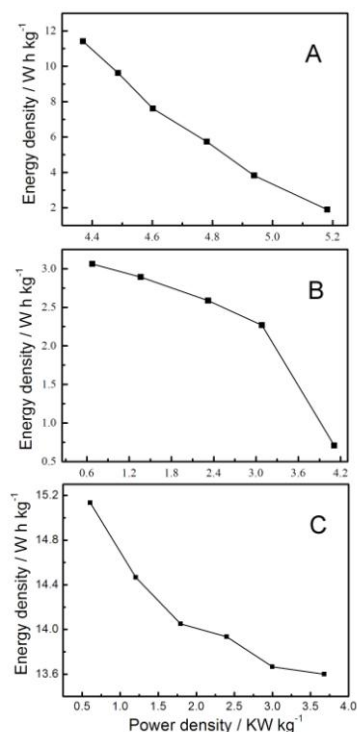


Figure 3. Specific power as a function of specific energy of P(EDOT-Fu) (A), P(Fu-EDOT-Fu) (B) and P(EDOT-Fu-EDOT) (C) films in monomer-free $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ (0.1 mol L^{-1}).

The energy density as a function of power density of furan-EDOT copolymers modified electrode was investigated, as shown in Fig. 3. From the above measurements, an energy density of 15

Wh kg^{-1} was obtained for P(EDOT-Fu-EDOT) electrode at a power density of 0.6 KW kg^{-1} , which was higher than those of P(EDOT-Fu) and P(Fu-EDOT-Fu) electrode. Even at a high power density of 13.6 KW kg^{-1} , the energy density still reached 3.7 Wh kg^{-1} , which exhibited a large power range that can be obtained while maintaining a relatively high energy density compared with P(EDOT-Fu) and P(Fu-EDOT-Fu) electrode. Besides, the specific energy of the furan-EDOT copolymer electrode also decreases with increasing charge-discharge current.

Since the specific capacitance of polymer electrode is related to the amounts of deposited copolymer films, the effect of furan-EDOT copolymer amounts on the specific capacitance were studied, as shown in Fig. 4. The specific capacitances of P(Fu-EDOT-Fu) and P(EDOT-Fu-EDOT) decrease with an increasing specific mass of copolymers, while that of P(EDOT-Fu) increases with an increase of copolymer films. This phenomenon that the specific capacitance of copolymer electrode decreases with the increase of copolymer films was due to the thickness of copolymer films increased with the mass loading when the surface area of the working electrode was fixed. The increase in thickness will induce the results as following: 1) increase in film resistance, 2) decrease the effective polymer contributing on specific capacitance value.

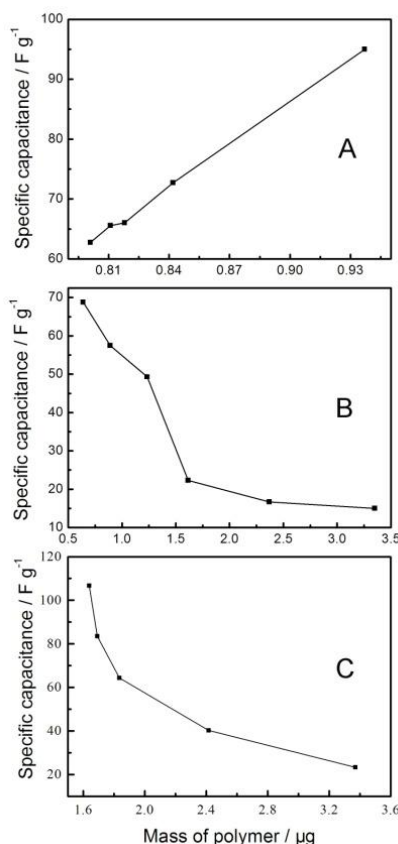


Figure 4. Specific capacitance of P(EDOT-Fu) (A), P(Fu-EDOT-Fu) (B) and P(EDOT-Fu-EDOT) (C) films in monomer-free $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ (0.1 mol L^{-1}) as a function of the mass, respectively.

By considering all the above data concerning electrochemical properties, it can be clearly observed that the capacitor performance of P(EDOT-Fu-EDOT) is superior to P(EDOT-Fu) and P(Fu-EDOT-Fu). We ascribe this situation to the following reasons: 1) By employing EDOT as the terminal groups (EDOT-Fu-EDOT), the copolymer exhibited better electronic properties than in the case of Fu as ending groups (Fu-EDOT-Fu and Fu-EDOT), mainly due to the electron-donating ethylenedioxy group in EDOT unit [41,42]. 2) Through increasing the chain length of monomers, the onset oxidation potential was successively decreased, making it a reality to obtain better polymer films at relatively low potentials. 3) Structural defects could probably be an inevitable factor due to the poor stability of furan units during the electropolymerization.

4. CONCLUSIONS

In this paper, a series of furan-EDOT copolymers have been successfully electrodeposited and evaluated as an active electrode material for supercapacitors. The specific capacitance of P(EDOT-Fu-EDOT) was 75 F g^{-1} at a current density of 1 A g^{-1} , which was higher than those of P(EDOT-Fu) (65 F g^{-1}) and P(Fu-EDOT-Fu) (46 F g^{-1}). The energy density of P(EDOT-Fu-EDOT) electrode was 15 Wh kg^{-1} at a power density of 0.6 W kg^{-1} , which was higher than those of P(EDOT-Fu) and P(Fu-EDOT-Fu) electrode. These results indicated that P(EDOT-Fu-EDOT) copolymer modified electrode showed superior supercapacitor properties than P(Fu-EDOT-Fu) and P(EDOT-Fu). These intriguing features make it a promising candidate as electrode material for supercapacitors.

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