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PPy modified titanium foam electrode with high performance for supercapacitor

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ABSTRACT

Pyrrole was polymerized on the surface of titanium foam using $FeCl_3$ as oxidant and the as-synthesized product could be directly used as electrode for supercapacitor. The globular polypyrrole (PPy) particles were firmly loaded on the substrate with high density. The morphology study of PPy film is observed in SEM images, the XRD, FTIR and UV–vis spectra reveal the structure and crystalline of PPy nanoparticles. The electrochemical properties of PPy modified electrode are investigated by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and cycle life techniques. The electrochemical measurements showed such a PPy–Ti electrode had a wide working potential window, a high specific capacitance of 855 $F\,g^{-1}$ and excellent cycle stability at a discharge current density of 1 $A\,g^{-1}$.

1. Introduction

Nowadays, the supercapacitors have been applied in many fields, such as energy storage battery, electric power system, electric vehicle, cordless telephone and others owing to their high power density, wide thermal operating range and long cycle life [1,2]. Currently, the main electrode materials for supercapacitor contain metal oxides, carbon and conductive polymers. Among them, the conductive polymer electrode materials, such as polypyrrole (PPy), polyaniline (PANI) and polythiophene, provide flexible mechanical behavior and excellent electrochemical oxidation and reduction property [3–5]. Especially, PPy is promising for its good electrical conductivity, high energy storage capacity and excellent environmental stability [3]. Many synthetic methods including electrochemical polymerization and chemical oxidation have been reported to generate kinds of PPy with different morphologies and components [6–8]. The PPy-based electrodes include various manners: the PPy can be deposited on various substrates, doped by different compounds and complexed with distinct materials [9–13].

The low cost, good mechanical resistance and corrosion resistant property of titanium make it the widely used material as the electrode substrate in the field of electrochemistry [14]. The porous and skeletal structure endows the titanium foam with large specific surface area which is in favor of quick electron transfer [15]. Therefore, different materials, including conductive polymers have been deposited on its surface for application of various fields. For example, PPy film on titanium could electrically controll drug release and exhibited a promising performance for biomedical applications [16]. PPy-coated titanium could also be implemented for the reduction of Cr(VI) to the less toxic trivalent state Cr(III) [17]. The kinetics of electrochemical polymerization of pyrrole in aqueous acidic nitrate solution on a passivated bare titanium electrode has been studied by Mokrane et al. [18].

In this article, we explored the *in situ* chemical synthesis of PPy particles directly grown on the titanium foam by using $FeCl_3$ as oxidant. PPy materials have been synthesized

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via different strategies, including the oxidation polymerization by $FeCl_3$ [7,19]. However, no reports were found to present the growth of PPy on the titanium foam without any adhesion agent at room temperature, which can be the directly used as electrode for supercapacitors. The *in situ* oxidation polymerization method was operated simply and the combination between PPy film and titanium foam was tightly [7]. The as-prepared electrode displayed high specific capacitance and excellent cycle stability.

2. Experimental

2.1. Reagents

Pyrrole monomer (Capchem, 99.8%) was purified by distillation under reduced pressure and stored at −5 °C before use. Ferric chloride ($FeCl_3 \cdot 6H_2O$), ammonium persulfate (APS) and other chemicals are reagent grade and used as received. Titanium foam with the edge thickness of ~1 mm was chopped into pieces with dimension of 10 mm × 10 mm and weight about 0.3 g. Then the titanium foam was cleaned consecutively in acetone, 6 M hydrochloric acid and deionized water. Finally, it was dried at 50 °C for 2 h.

2.2. Preparation of PPy film on titanium foam

Two milliliter of pyrrole (0.1 M) and 2 mL of $FeCl_3 \cdot 6H_2O$ (0.1 M) solution were mixed in a centrifugal tube containing a piece of cleaned titanium foam. After a certain period of reaction time, the titanium foam loaded with PPy was taken out and cleaned with deionized water. Finally, it was dried at 40 °C for 3 h.

2.3. Characterization and electrochemical measurements

The morphology of the PPy on titanium foam was determined by a field-emission scanning electron microscopy with an accelerating voltage of 5 kV (FE-SEM, JSM-6700F, JEOL, Japan). The measurement of the crystalline feature was analyzed by X-ray powder diffraction (XRD, SHIMADZU XRD-6000) on a Ni-filtered Cu Kα radiation at 40 kV and 200 mA with the 2θ ranging from 10° to 40° and step scan rate of 10° min^{-1}. Fourier transform infrared spectrum of the PPy particles that was peeled off from titanium foam was obtained in the 4000–500 cm^{-1} range (FT–IR, AVATAR360, Nicolet). UV–Vis spectroscopy of the PPy particles was investigated in ethanol solution (UV-2400PC).

The electrochemical performance of PPy modified electrodes was evaluated by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) techniques in a three-electrode system containing the PPy modified titanium foam as working electrode, a saturated Hg/Hg_2Cl_2 electrode (SCE) as reference electrode and a counter electrode of platinum sheet that possesses the same area as working electrode. The distance between the working and counter electrodes was nearly 10 mm. 0.5 M K_2SO_4 as the electrolyte was deoxygenated with a stream of N_2 before use. CV was measured in a potential range of −1–0.5 V (vs. SCE) at changed scan rates, and GCD curves were investigated at step increasing current densities with the initial voltage of −0.5 V to the final voltage of 0 V. The above electrochemical tests were taken on a CHI 660D electrochemical workstation.

The symmetrical two-electrode cells are assembled with PPy modified titanium foam and blank titanium foam for the long term cycle stability test on Battery testing system (Neware), and the distance between the two electrodes was 1 mm.

3. Results and discussion

3.1. Physicochemical characterization

The SEM images of the PPy modified electrode are presented in Fig. 1. Compared with the blank titanium foam (Fig. 1A), a large number of PPy particles are observed on the titanium foam surface (Fig. 1B). These particles link with each other to form a network structure (Fig. 1C) and this enables facile contact between the electrode materials and the electrolyte for the redox reactions and a high specific capacitance may be achieved thereby [10]. A higher-magnified image in Fig. 1D exhibits that the PPy particles have a diameter ranging from 400 to 500 nm.

The XRD pattern of the PPy modified electrode is presented in Fig. 2 curve b, the two strong peaks located at $2\theta = 35.2°$ and 38.5°can be attributed to the Ti (JCPDS 44-1294) metal crystal for all the substrates of electrodes [20,21]. By contrast with the XRD pattern of blank titanium foam in curve c, the weak wave appearing at 2θ value from 18° to 25° is identified to the presence of PPy film on the titanium foam. A clearer observation on the separated PPy powders scraped from the substrate confirms the amorphous PPy phase (Fig. 2, curve a) [19].

Fig. 3 exhibits the FT–IR spectrum of the PPy powder. The absorption bands at 1429 and 1538 cm^{-1} are assigned to the C=C and C—N stretching vibrations of PPy chain, respectively [8]. The peaks at 1037, 1192 and 1305 cm^{-1} are the characteristic peaks of in-plane vibrations of C—H [7,19], while the peak at about 913 cm^{-1} represents the C—H out-of-plane anamorphic vibrations of the PPy ring [22].

The UV–visible spectrum of PPy powder is shown in Fig. 4. The absorption at around 525 nm is associated with the polaron state of pure PPy [23]. The free carrier tail after 600 nm is associated with the delocalization of electrons in the polaron band, promoted by the stiffening extension of polymer chain [24].

3.2. Electrochemical characterization

To research the electrochemical performance of the PPy modified electrode, CV and GCD techniques were carried out in the three-electrode system. Eq. (1) is used to calculate the specific capacitance of the electrode based on the CV curves.

$$C = \int i \frac{dt}{dv} \tag{1}$$

where i is the current, t is the time and v is the voltage. Therefore, we could simply compare the capacitances from the different CV areas [25].

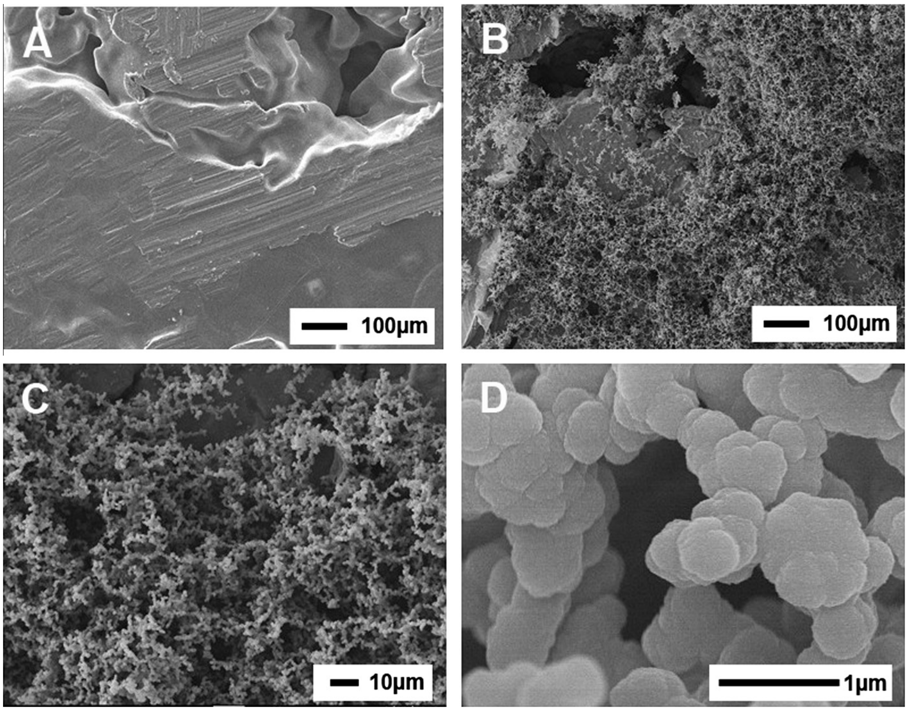

Fig. 1. (A) SEM image of blank titanium foam. (B–D) SEM images of PPy modified titanium foam electrode with different magnification.

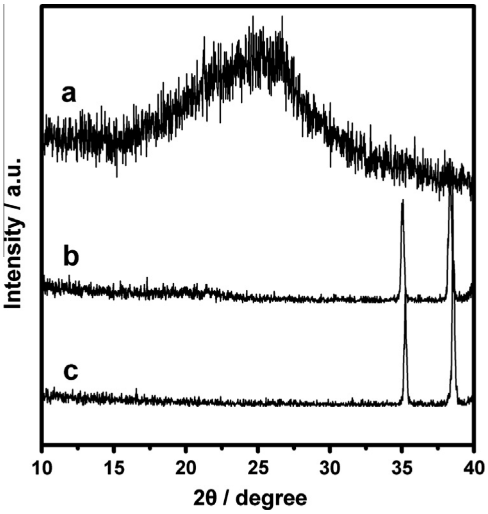

Fig. 2. XRD patterns of PPy powder (a), PPy modified titanium foam electrode (b) and blank titanium foam (c).

The discharge capacitance C is calculated from the immediateness line of the discharge curves in the GCD measurement using the following equation:

$$C_m = \frac{C}{m} = \frac{i\Delta t}{\Delta V_m} \quad (2)$$

where i is the charge–discharge current, Δt is the discharge time, m is the mass of active material on the electrode that excludes the weight of titanium substrate and ΔV is the voltage drop in the discharge process [26].

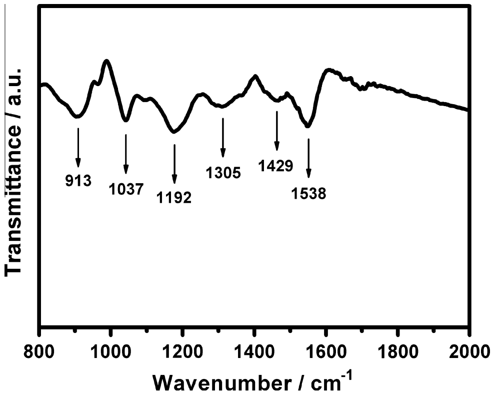

Fig. 3. FTIR spectrum of PPy powder on the electrode.

The CV curve of the PPy modified electrode is shown in Fig. 5A, which is achieved at a scan rate of 20 mV s^{-1}. It appears a couple of redox waves of PPy functional groups, where the cathodic wave at about −0.5 V and the anodic wave at about −0.23 V are owing to the insertion and expulsion of K^+ ions in the electrolyte [12]. It is also noted that the weak oxidation wave at about 0.3 V is attributed to the insertion of SO_4^{2-} ions during the electrolysis process. While the pair redox peaks of −1 and 0.5 V is related to the OH^-/H^+ adsorption/desorption on the electrode surface [26]. The nearly flat curve of the blank titanium foam illuminates no remarkable electrochemical reaction between the substrate and the electrode.

The CV curves of the PPy modified electrodes obtained from different reaction time of 8 h, 12 h, 16 h and 20 h at

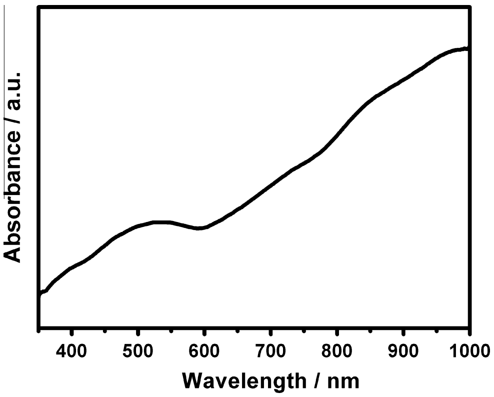

Fig. 4. UV–vis spectrum of PPy powder on the electrode.

scan rate of 20 mV s^{-1} are shown in Fig. 5B. In the same potential range of these electrodes, the wider range of current density indicates the higher pseudo-capacitance according to the Eq. (1). Therefore, based on the biggest CV area, we selected the sample with reaction time of 12 h for the next experiment.

Fig. 5C shows the CV curves of PPy modified electrode from reaction time of 12 h at various scan rates of 10, 20, 50 and 100 mV s^{-1}. As the scan rate increases, the effective interaction between the electrode and the ions decreases seriously, and the deviation from the shape of CV becomes obvious. It is seen that the redox current increased with increasing scan rate, indicating a good rate capability of our PPy electrode. Meanwhile, the cathodic peak potential shifts toward more positive direction and the anodic peak potential shifts oppositely with the increasing scan rates. The reason is that the high scan rate causes the quick diffusion of electrons and counterions between the electrode and the electrolyte during potential cycling. Besides, the porous structure of the surface of PPy modified electrode could promote the diffusion of counterions [11].

Fig. 5D displays the galvanostatic charge–discharge curves of PPy modified electrode from reaction time of 12 h in 0.5 M K_2SO_4 electrolyte. The GCD curves behave mirror-like shape, indicating a good supercapacitor property. The calculated specific capacitances at increasing discharge current densities of 1, 2, 5 and 10 A g^{-1} are 855, 627, 356 and 160 F g^{-1}, respectively. The IR drop of the electrode is small, which may result from the good transport of electron and counterions between the electrode and electrolyte [11]. It should be noticed that the outstanding specific capacitance of 855 F g^{-1} of PPy modified electrode is higher than that of other reported PPy-based electrodes, for instance, RuO_2–PPy (302 F g^{-1}), single walled carbon nanotubes-PPy (131 F g^{-1}), MnO_2–PPy (620 F g^{-1}) and [13,27,28].

We consider the high specific capacitance should originate from the following two reasons: (1) the porous

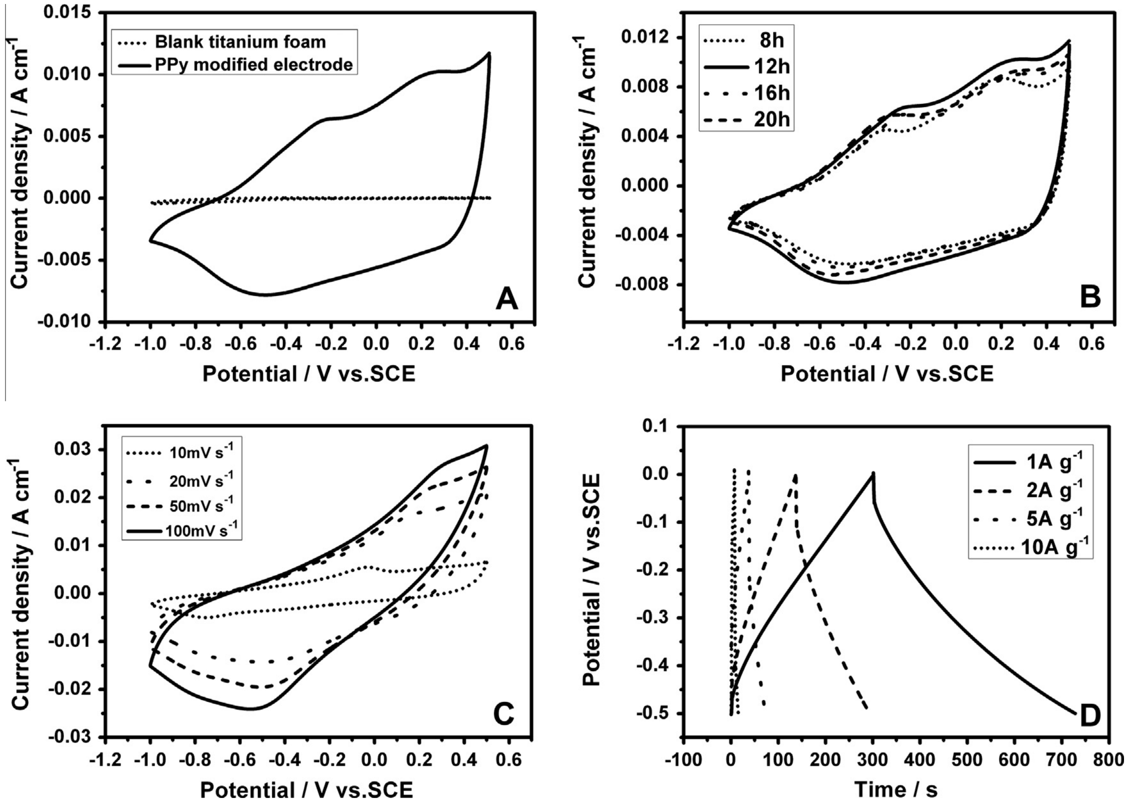

Fig. 5. (A) The CV curves of blank titanium foam and PPy modified electrode at scan rate of 20 mV s^{-1}. (B) The CV curves of PPy modified electrode of 8 h, 12 h, 16 h and 20 h reaction time at scan rate of 20 mV s^{-1}. (C) The CV curves of PPy modified electrode of 12 h reaction time at different scan rates of 10, 20, 50 and 100 mV s^{-1}. (D) The GCD curves of PPy modified electrode of 12 h reaction time at increasing current densities of 1, 2, 5 and 10 A g^{-1}.

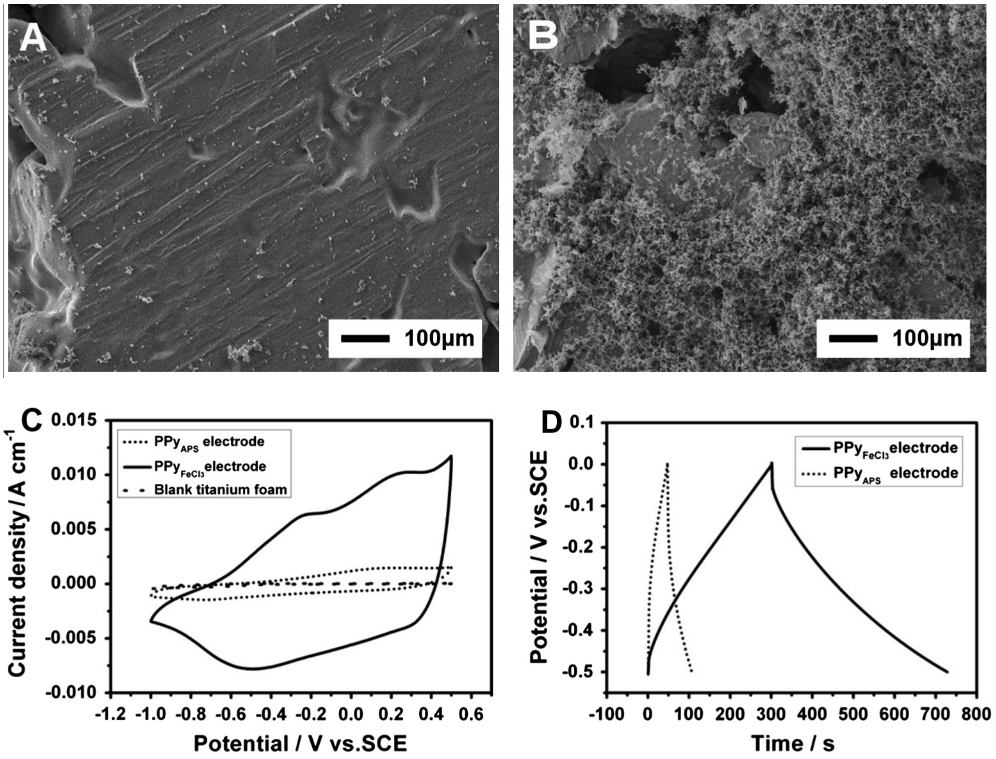

Fig. 6. (A and B) SEM images of PPy_{APS} and PPy_{FeCl3} electrodes. (C) The CV curves of PPy_{APS}, PPy_{FeCl3} electrodes and blank titanium foam at scan rate of 20 mV s^{-1}. (D) The GCD curves of PPy_{APS} and PPy_{FeCl3} electrodes at the current density of 1 A g^{-1}.

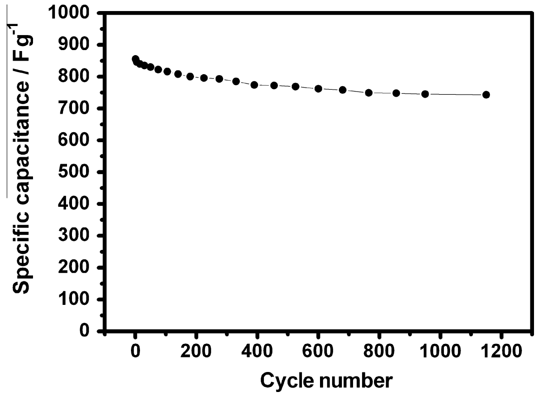

Fig. 7. Variation of specific capacitance as a function of cycle number about 1150 cycles for PPy modified titanium foam electrode in the 0.5 M K_2SO_4 electrolyte at a discharge current density of 1 A g^{-1}.

network structure of the PPy on the titanium substrate, which allows facile contact and redox reaction between electrode and electrolyte (Fig. 1C); (2) the strong interaction between PPy and the substrate that can provide good conductivity for electron transport (Fig. 5D). As a control experiment, we prepared the PPy modified electrode using ammonium persulfate (APS) as oxidant (see Supporting Information). For convenience, the two kinds of electrodes are named as PPy_{FeCl3} and PPy_{APS}. Compared with the PPy_{FeCl3} electrode, few particles were observed on the substrate in PPy_{APS} electrode (Fig. 6A and B). Furthermore, the electrochemical tests including CV and GCD show that the PPy_{APS} electrode presents inferior performance to PPy_{FeCl3} electrode, as can be seen in Fig. 6C and D. APS is a widely used oxidant for polymerization of pyrrole, and it behaves a higher redox potential than that of $FeCl_3$ (2.05 vs. 0.771 V). Such a high oxidant ability does make a fast polymerization, but it also leads to the oxidization of titanium surface, which greatly weakens the attachment of PPy on the substrate.

As an efficient pseudo-capacitive material, the stability towards electrochemical cycling of the PPy modified titanium electrode plays an important role in the electrochemical characterization. Fig. 7 shows the sequential charge–discharge cycling of 1150 cycles in 0.5 M K_2SO_4 electrolyte at a current density of 1 A g^{-1}. In consideration of the 1st cycle's specific capacitance of 855 F g^{-1}, the capacitance decreases in the first 200 cycles, retaining 89.8% of the initial value (768 F g^{-1}) and keeps stable from 768 to 756 F g^{-1} for the following 950 cycles. It seems that the initial 10.2% decline may be related to the loss of unstable PPy particles by dissolution in the electrolyte solution [28,29].

4. Conclusions

The corrosion resisting and porosity property are the superiorities of the titanium foam as the electrode in the field of supercapacitors. Thereupon, we synthesized PPy particles in $FeCl_3$ oxidation solutions on the surface of titanium foam. By contrast with the PPy_{APS} electrode and other PPy-based electrodes, the PPy_{FeCl3} electrode shows good electrochemical property in cyclic voltammetry and galvanostatic charge/discharge measurements. The admirable electrochemical performance and the excellent cycle stability would lead the PPy modified electrode to be a promising material for making electrodes of polymer supercapacitors.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.eurpolymj.2013.08.001.

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