Int. J. Electrochem. Sci., 4 **(2009)** 1541 - 1547

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

Porous Polypyrrole Prepared by Using Nanoscale Calcium Carbonate as a Core for Supercapacitance Materials

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Received: 23 October 2009 / *Accepted:* 11 November 2009 / *Published:* 1 December 2009

A porous polypyrrole has been synthesized via nanoscale calcium carbonate used as a core. The morphology and pore structure of as-prepared polypyrrole have been characterized by transmission electron miscroscopy. The porous polypyrrole shows high electrochemical performance in an alkaline electrolyte of 1mol L^{-1} KOH and the specific capacitance is up to 650 F g^{-1}. The measurement of cyclic life indicates that the porous polypyrrole is more stable than conventional polypyrrole in alkaline solution and the probable reasons are proposed.

Keywords: Porous polypyrrole; Specific capacitance; Calcium carbonate; Core

1. INTRODUCTION

Electronically conducing polymers (ECPs) have been intensively studied in the past decades [1-6]. ECPs, such as typical polypyrrole (PPy), polyaniline (PAni) and polythiophene (PTh), have been prepared via chemical or electrochemical methods. Among them, conducting polypyrrole has been the focus of a great deal of research for supercapacitor application in recent years [7–11] because of high electric conductivity in doped state, high specific capacitance, good chemical and thermal stability, environmentally friendly properties and facile synthesis especially [12]. However, the electrochemical activity of PPy in dedoped state is very low and considerable capacitance will drop off within a short period, greatly impeding their ability to function in a long-term implant. Furthermore, the specific capacitance of PPy in previous reports is relatively low in the range of 90-480 F g^{-1} [9, 13-15]. These problems could inhibit PPy as electrode materials in practical application.

In order to prompt the charge storage capacity of a polymer, Chen et al. have tried to thicken the film of ECPs. However, for conventional PPy electrode, increasing the film thickness deteriorates the electronic performance [16]. Therefore, some attentions focus on the porous PPy. Naegele and Brittihn have prepared a porous PPy structure with large specific surface area, being the prerequisite for high-power application due to quick charging-discharging rate [17]. Li et al. have synthesized polypyrrole thin films with pores in nanometer scale, exhibiting high conductivity (20.5 S cm^{-1}) [18]. A controllable pore-size CNTs/PPy composite has been prepared by Kim et al., performing specific capacitance of 250 F g^{-1} [19]. Graeme's group developed a porous conducting polymer/heteropolyoxometalate hybrid material that shows high specific capacitance (210 F g^{-1}) and low ionic resistance [20]. Fan and Maier have used an electrodeposition method to obtain a porous nanostructured polypyrrole, which has high specific capacitance up to 480 F g^{-1} [15]. However, the above-mentioned methods are complicated, or costly or non-environmentally friendly and it is difficult to prepare large-scale porous polymer. Therefore, low-cost and facile methods are still needed to explore.

Herein, we have used nanoscale calcium carbonate as core, and then pyrrole has been polymerized on its surface using ferric chloride hexahydrate as oxidant. Owing to the release of CO_2 when calcium carbonate is dissolved in weak acidic system, the nanostructured pore is fabricated within PPy. The electrochemical measurements reveal that porous PPy performances higher specific capacitance and longer cyclic life in alkaline electrolyte.

2. EXPERIMENTAL PART

2.1. Chemical reagents

Pyrrole monomer (98%, Aldrich Chemical Co.) was purified by distillation under reduced pressure and then stored under nitrogen in a refrigerator until use. Sodium 4-methyl benzene sulfonate (TsONa) was purchased from Sinopharm Chemical Reagent Co. Ltd, Shanghai, China. The diameter and BET surface area of the nanoscale calcium carbonate is 80 nm and 25 m^3 g^{-1}, respectively. Other chemicals were of analytical reagent grade without further purification.

2.2. Synthesis of the porous PPy

The porous PPy (denoted as PP) was synthesized by chemical oxidative polymerization. First, 0.80 g $CaCO_3$, 0.40 g TsONa, 45 g $CaCl_2$ and 20 mL ethanol were put into 40 mL distilled water with magnetic stirring in N_2 atmosphere for 30 mins, then added 0.5 mL pyrrole by a syringe. After 10 mins, 60 mL of 0.2 mol L^{-1} $FeCl_3$ solution was slowly dropped into the reaction vessel. The polymerization was carried out for 12 h in an ice-bath with the maintained magnetic stirring under N_2 atmosphere. The suspension of PPy was filtered and rinsed several times with distilled water and ethanol to remove retained Py monomer and oxidant. Then the as-prepared powder was transferred into HCl solution for $CaCO_3$ removal for 24 h. The mixture was filtered and rinsed several times again with distilled water. After that the porous PPy was dried in vacuum at 60 ℃ for 12 h. For comparison, the conventional PPy was synthesized similarly as PP. The difference is the no addition of $CaCO_3$.

2.3. Structure characterization

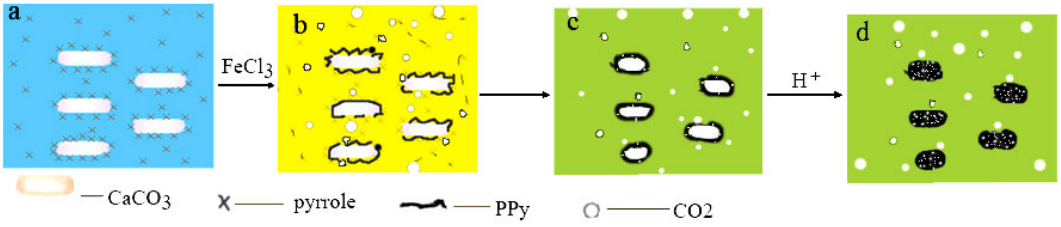
The morphology and pore structure of as-synthesized PPy were characterized using a transmission electron microscope (TEM, Philips TECNAI-10, 100 kV).

2.4. Electrochemical performance

The electrochemical behaviours of PP and PPy were investigated with CHI 660B electrochemical workstation (CHI, Shanghai, China). A three electrode system, which consists of a working electrode, a Ni foil auxiliary electrode and Hg-HgO reference electrode, was used for electrochemical measurements. The working electrode was prepared by pressing the mixture of active materials and carbon black (6:1 wt %) into a foam nickel electrode under 35 MPa. The electrochemical solution was not deaerated by N_2 bubbling and maintained in ambient atmosphere throughout the experiment. Different scan rates were employed in cyclic voltammetry in the range of -0.7 to 0.1 V vs. Hg-HgO. Different constant-current densities were employed for charge/discharge measurement.

3. RESULTS AND DISCUSSION

Because the $FeCl_3$ solution is acidic, the nanoscale calcium carbonate will be quickly dissolved in the $FeCl_3$ solution. In order to avoid this phenomenon, the additional $CaCl_2$ is added into the reaction system. The abundant $CaCl_2$ inhibits the dissolution of $CaCO_3$, therefore, $CaCO_3$ is slowly dissolved and CO_2 forms and releases slowly. Thus, the nanoporous PPy was easily obtained. The procedure is illustrated by Scheme 1.



Scheme 1. Schematic illustration of the procedure for preparation of porous PPy.

A typical morphology of PPy have been investigated using TEM, as shown in Fig. 1. Fig. 1 a shows the surface of PP is rough and irregular, PP with the diameter of 50-100 nm is smaller than that of conventional PPy (100-200 nm) [15]. The formation of the smaller particles could involve: the pyrrole monomer had been absorbed at the surface of $CaCO_3$ when it was put into the solution, the particles of $CaCO_3$ became the polymerization centers (see Scheme 1 a and b). With the decrease of $CaCO_3$ particles in acidic environment, the diameter of porous PPy became smaller (Scheme 1 c and d). On the other hand, the surface of $CaCO_3$ is irregular and rough, as supported by TEM, resulting in the irregular and rough surface of PP. The rough surface and pore structure play a crucial role for higher specific surface area. These will be advantageous to increase charge storage. A large-magnification TEM image reveals PP contains nanoporous structure, as shown in Fig.1b.

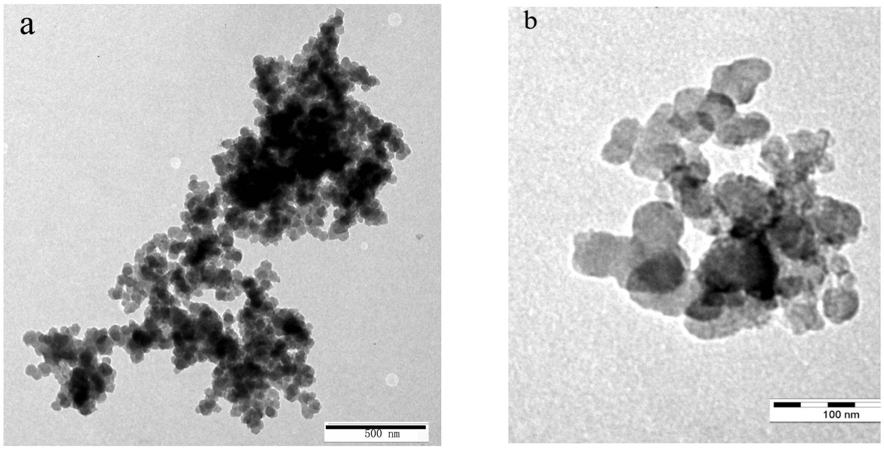


Figure 1. Low-magnification (a) and large-magnification (b) TEM images of PP.

We have utilized cyclic voltammetry and galvanostatic charge/discharge technique to measure the electrochemical performance of the as-prepared PPy. Fig. 2a presents the cyclic voltammograms (CVs) of PP and PPy electrodes measured in 1mol L^{-1} KOH electrolyte solution at a scan rate of 2 mV s^{-1}. It can be seen that a clear deviation between the peak of reduction and oxidation indicates that polypyrrole is a typical pseudocapacitance material. Obviously, the specific capacitance of PP is larger than that of PPy, and the specific capacitance calculated from CVs of PP and PPy is 650 F g^{-1} and 572 F g^{-1}, respectively. A probable mechanism for redox reaction of PPy is as follows: the α-C atoms on the PPy rings have been almost oxidized to form C-C bonds in the process of polymerization, therefore, only some α-C atoms at the end of the polymer chains and β-C atoms of the PPy chains could be oxidized or deoxidized. When the scan rate was low, these α-C atoms and β-C atoms are not only oxidized and deoxidized, but also the doping ions have enough time into/eject from PPy particles freely. Therefore, the specific capacitance of PP and PPy is high. CVs of PP and PPy at different scan rates are shown in Fig. 2b and c. Increasing scan rates, the specific capacitance of two kinds of polypyrroles drops down to 262 F g^{-1} and 182 F g^{-1} at scan rate of 50 mV s^{-1}, respectively(see Fig. 2d). The specific capacitance of PP is larger than that of PPy because PP with nanoporous structure makes the doping ions enter into/eject from PPy more easily [12].

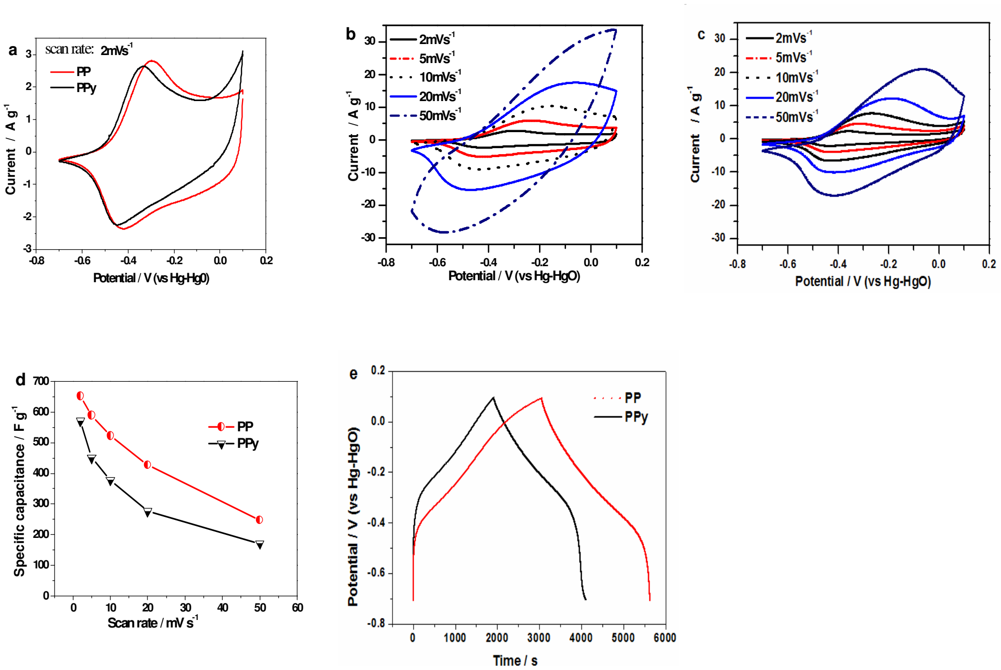


Figure 2. (a) CVs of PP and PPy in 1mol L^{-1} KOH electrolyte solution at a scan rate of 2 mV s^{-1}; CVs of PP (b) and PPy (c) at the different scan rates; (d) Dependence of specific capacitance vs scan rates of the PPy and PP; (e) Charge/discharge curves of PP and PPy at current densities of 0.2 A g^{-1}.

Fig. 2 e show the galvanostatic charge/discharge curves of PP and PPy electrode at a current density of 0.2 A g^{-1}. The specific capacitance (C_m) can be calculated according to Eq. (1) [3]:

$$C_m = \frac{C}{m} = \frac{i\Delta t}{\Delta V m} \qquad (1)$$

where i, Δt, ΔV and m are the charge/discharge current, the discharge time, the electrochemical window (0.8V) and the mass of active material within the electrode (6.3mg). The specific capacitance of PP and PPy calculated from Fig. 2e is 643.3 F g^{-1} and 548.5 F g^{-1}, being consistent with the capacitance of the CVs.

The stability of the PP and PPy in alkaline electrolyte was also performed by cycle-life measurement (Fig. 3 a and b). Owing to charging-discharging process, C atoms have been oxidized to become C-OH [21], therefore, there is coordination bond between the C^+ and :OH (see Fig. 3d), this bond makes the C atom decrease positive charge not to accept electron facilely, causing the drop-off of the specific capacitance. As shown in Fig. 3c, after 1000 cycles, the dissipation of specific capacitance for the PPy is 87 % and only 60 % for the PP. This illustrates that the PP is much more stable than PPy because the specific surface area of PP is larger than that of PPy which can be testified by nitrogen adsorption-desorption measurements. Higher surface can absorb more TsO anion and Cl anion to form a compact negative layer, which can block off the attack of OH anion, therefore, the stability of the PP in the alkaline solution increase and relatively higher specific capacitance is retained.

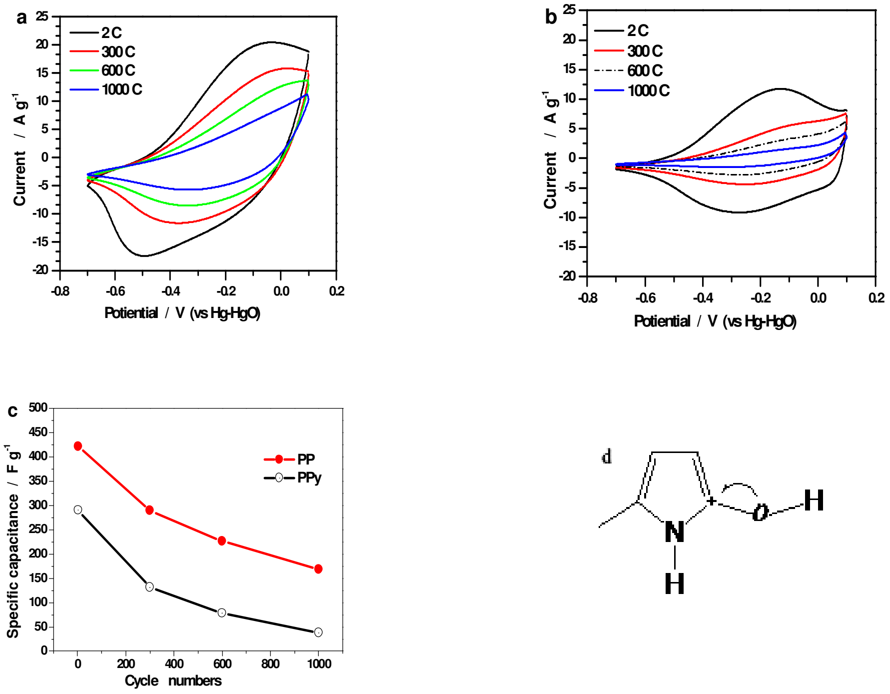


Figure 3. CV curves of PP (a) and PPy (b) in 1mol L^{-1} KOH electrolyte at 20 mV s^{-1} from 2 to 1000 cycles; (c) The dependence of specific capacitance vs cycle numbers of PPy and PP; (d) The coordination bond between the C^+ and :OH.

4. CONCLUSIONS

Porous PPy with higher specific capacitance has been prepared by using nanoscale calcium carbonate as core, the porous PPy exhibits higher stability in alkaline solution than conventional PPy. The structure of the porous PPy could be simply adjusted by the change of the mass and nanosize of nanoscale calcium carbonate. Indeed, such versatile method could be extended to other conducting polymers such as polyaniline and polythiophene.

ACKNOWLEDGMENTS
The authors wish to acknowledge financial support from the Natural Science Foundation of China (20876067) and the Young-teacher Fund of Jinan University (51208023).

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