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Short communication

Synthesis and pseudo-capacitance of chemically-prepared polypyrrole powder

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Abstract

The effect of the solvent used in the chemical polymerization of pyrrole on the electrochemical pseudo-capacitance properties of the material is investigated by means of cyclic voltammetry. Electro-conducting polypyrroles (PPy) are prepared in the presence of various solutions such as H_2O, diethyl ether, and acetonitrile (ACN). The PPy powder prepared in H_2O exhibits the largest capacitance value, approximately 355 F g^{-1}, in ACN solution containing 1 M tetraethylammonium tetrafluoroborate ($TEABF_4$). This dependency on solvent is directly related to the surface roughness of PPy powder.

Keywords: Cyclic voltammetry; Electrochemical capacitor; Electro-conducting polymer; Polypyrrole; Pseudo-capacitance; Surface roughness

1. Introduction

Many workers have extensively studied electrochemically polymerized electroactive polypyrrole (PPy) because it is a promising electroactive material for a double-layer supercapacitors and secondary batteries due to its high redox and capacitive current [1–15].

There are, however, some limitations to the use of electrochemically polymerized PPy films as practical electrodes. For example, it is difficult to use a slurry method for coating on to an aluminum foil current-collector. By contrast, chemically polymerized PPy powder offers advantages, namely, mass-production is very easy and the slurry coating method allows application of the powder to aluminuim current-collectors.

In this study, the pseudo-capacitance properties of PPy powder chemically prepared in various solvents are examined. The relationship between capacitance and surface roughness is discussed.

2. Experimental

2.1. Materials

Pyrrole (Aldrich, 99%) was distilled prior to use. All manipulations and reactions involving anhydrous ferric chloride (Aldrich, 98%) as an oxidant were carried out under a dry nitrogen atmosphere. Sodium *p*-toluenesulfonate (Aldrich, 98%) was used without any purification as a surfactant for the chemical polymerization of pyrrole. All other reagents and solvents were obtained from commercial sources and were used as received.

2.2. PPy chemical synthesis

2.2.1. Reaction of pyrrole with H_2O

H_2O (100 ml) was added to 3.35 g (0.5 M) of pyrrole and 3.88 g (0.2 M) of sodium *p*-toluenesulfonate in a round-bottom flask which contained a magnetic stirrer. H_2O (20 ml) was added to 3.24 g (1 M) of $FeCl_3$ and then introduced in a single portion to the stirred pyrrole/H_2O solution. Upon addition of the $FeCl_3$, a reaction exotherm was noted and the solution instantly acquired a black colour as the precipitate of PPy formed. After a reaction time of

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Table 1
Conductivity of PPy prepared in different solvents

Solvent	Conductivity (S^{-1} cm)
H_2O	1.25
Diethyl ether	3.50
Acetonitrile	9.5

6–8 h at 22 °C, the mixture was filtered and the precipitate was washed with copious amounts of distilled water. The black powder was dried in vacuum (60 °C, 5 h) to yield 1.1 g of polymer. The conductivity of this polymer was in the range 1.0–1.4 S^{-1} cm (Table 1).

2.2.2. Reaction of pyrrole with diethyl ether

This compound was prepared by a method similar to that used above, but diethyl ether was used instead of water as the solvent. The conductivity value of this polymer was in the range 3.25–3.75 S^{-1} cm.

2.2.3. Reaction of pyrrole with acetonitrile

This compound was prepared by a method similar to that above, but with acetonitrile (ACN) as the solvent. The conductivity was in the range 9.0–10.5 S^{-1} cm.

2.3. PPy electrode preparation

The PPy with Super-P as an electrical conductive agent was uniformly ground to obtain a fine powder. Teflon powder was added to this mixture as a binder. The resulting material was coated on to a stainless-steel metal cloth (1 cm × 1 cm), and then pressed into a 4 mm disc by roll pressure.

2.4. Electrochemical and electrical properties

The electrochemical properties of PPy were determined by means of cyclic voltammetry in acetonitrile that contained 1 M tetraethylammonium tetrafluoroborate ($TEABF_4$). The potential was scanned from −1 to +1 V and the scan rate was fixed at 5 mV^{-1} s. A plate and the silver wire were used as counter and pseudo-reference electrode, respectively. Conductivity data were obtained at 22 °C by using four-probe method.

3. Results and discussion

Scanning electron micrographs of the PPy powder prepared with different solvents are shown in Fig. 1. It is clearly seen that the degree of surface roughness of the PPy powder increases with the solvent used in the order: H_2O > diethyl ether > ACN. The surface of PPy powder prepared in ACN solvent has a much denser structure than that of powder obtained in either H_2O or diethyl ether. Since the morphology of PPy is strongly dependent on the solvent used in the polymerization, it is concluded that this behaviour is

(a)

(b)

(c)

Fig. 1. Scanning electron micrographs of PPy surface prepared in different solvents: (a) H_2O, (b) diethyl ether, (c) acetonitrile.

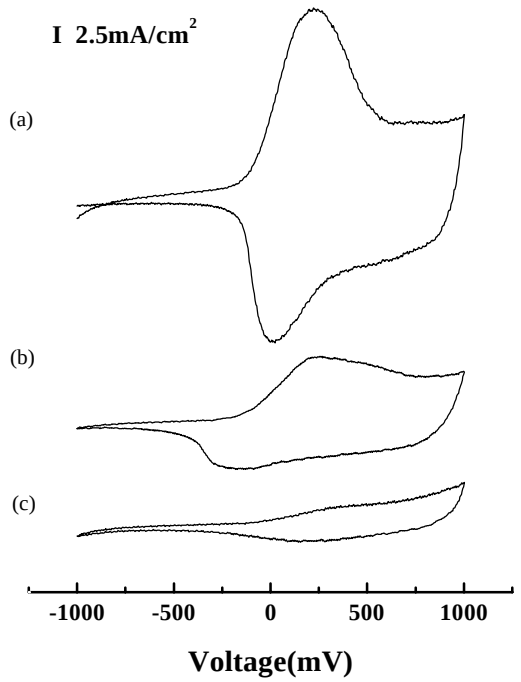

Fig. 2. Cyclic voltammograms of PPy electrode prepared in different solvents. Voltammograms obtained in acetonitrile solvent with 1 M $TEABF_4$ as supporting electrolyte; scan rate = $5\,mV\,s^{-1}$. (a) H_2O, (b) diethyl ether, (c) acetonitrile.

due to PPy solubility and solvent polarity. These findings are in agreement with previous results [16], and show that the morphological properties of PPy powder can be controlled through choice of the solvent.

Cyclic voltammograms to measure the electrochemical pseudo-capacitance of PPys prepared in the different solvents are presented in Fig. 2. The electrochemical parameters and specific pseudo-capacitance (C) are summarized in Table 2. The pseudo-capacitance values were calculated from the voltammograms by means of the following equation:

$$C = i\frac{dt}{dV} \quad (1)$$

where i is current in the capacitive potential region, and dt/dV is the reciprocal of the scan rate. It is found that the PPy powder prepared in H_2O system is electrochemically more reversible than the powder prepared in ACN or diethyl ether solution, as demonstrated by the well-defined shape of the voltammogram (Fig. 2(a)). This result means that the ion diffusion for charge compensation during the redox reaction is much faster in the porous structure of PPy prepared in H_2O than in the dense structure of the PPy prepared in either diethyl ether or ACN. The specific pseudo-capacitance of PPy prepared in H_2O is about $355\,F\,g^{-1}$.

Table 2
Electrochemical parameters of PPy prepared in different solvents

Solvent	$I_{p,a}$ [a]	$I_{p,c}$ [b]	$E_{p,a}$ [c]	$E_{p,c}$ [d]	Specific capacitance ($F\,g^{-1}$)
H_2O	26	−22	231	20	355
Diethyl ether	9	−7	236	−154	151
Acetonitrile	2	−3	356	157	55

[a] Oxidation peak current density ($mA\,cm^{-2}$).
[b] Reduction peak current density ($mA\,cm^{2}$).
[c] Oxidation peak potential (mV).
[d] Reduction peak potential (mV).

4. Conclusion

The specific capacitance of PPy powder decreases for samples prepared in H_2O, diethyl ether and ACN, respectively. The PPy prepared in H_2O has a capacitance of about $355\,F\,g^{-1}$ in ACN solution containing 1 M $TEABF_4$. This dependency on the solvent that is employed is related directly to the surface roughness of the resulting PPy.

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