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Improvement of capacitive performances of symmetric carbon/carbon supercapacitors by addition of nanostructured polypyrrole powder

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HIGHLIGHTS

- Nanostructured PPy powder is a beneficial additive in symmetric C/C supercapacitors.
- Specific capacitances were carefully evaluated using two electrochemical methods.
- A porous electrode model is more adequate than a diffusion model to fit EIS spectra.
- PPy powder allows an increase of the specific capacitance of composite electrodes.
- It leads to a lower charge transfer resistance at the separator/electrode interface.

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ABSTRACT

A nanostructured polypyrrole powder was synthesized in a previous work from the oxidation of pyrrole by a nanostructured MnO_2 powder used simultaneously as an oxidizing agent and a sacrificial template in a redox heterogeneous mechanism. In this study, this original PPy powder was used as an active additive material with different ratio in carbon/carbon symmetrical supercapacitors whose performances were studied by cyclic voltammetry and electrochemical impedance spectroscopy (EIS) using a Swagelok-type cell. From the EIS spectra, the complex capacitance was extracted using a model involving two Cole–Cole type complex capacitances linked in series. The specific capacitance values evaluated by EIS and cyclic voltammetry are in a good agreement between them. The results show that the addition of nanostructured polypyrrole powder improves significantly the specific capacitance of the carbon electrode and consequently the performances of carbon/carbon supercapacitors. The original and versatile synthesis method used to produce this polypyrrole powder appears to be attractive for large scale production of promising additives for electrode materials of supercapacitors.

1. Introduction

In recent years, electrochemical supercapacitors have attracted great attention because of their high capacitance and potential applications in energy storage. Electrochemical capacitors are indeed used to store the energy within the electrochemical double layer determined by the surface area and pore size distribution [1–3].

Activated carbon-based nanostructured materials with high specific surface areas are widely recognized as electrode materials for electric double-layer capacitors (EDLC). These products present outstanding properties, such as good electrical conductivity and stability, high accessible surface area, and reasonable cost [4–10]. Moreover, they can be produced in various forms, which allows the tuning of their porosity and their surface functionalization. Whether their electrical double layer is charged in aqueous or organic electrolytic solutions, their capacitance appears to be closely related to the surface area of the carbon/electrolytic solution interface. Moreover, it has been shown in literature over the last years that a good fit between their pore size and the size of electrolyte ions is beneficial for their performances. More accurately, it appears that 0.7–0.9 nm pore diameters are the most suitable for

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electrical double layer charging of pore walls with non-solvated ions in activated carbon materials. Even if additional mesopores interconnected with the above mentioned ultramicropores were shown to be beneficial for a good charge propagation, energy densities of carbon-based supercapacitors were often found to be lower than that of redox supercapacitors [5].

Recently, many research works have focused on additive electrode materials for supercapacitors, including conducting polymers and transition metal oxides to improve the capacitive performances of activated carbons [11–15]. In particular, many studies were focused on the synthesis and electrochemical characterisations of electronically conducting polymers, which represent promising electrode materials for the application of supercapacitors due to their high specific capacitance [11,14,15]. Among the conducting polymers, polypyrrole (PPy) is considered as an interesting material for supercapacitor electrodes due to its high conductivity, good redox reversibility, long-term environmental friendliness, low cost, and easy chemical or electrochemical synthesis [16,17]. Chemical synthesis of conducting polymers is simply achieved by oxidation of corresponding monomers using an oxidizing agent and thus is well adapted for mass-production in industry as it provides a cheap and efficient route [18,19]. Compared to bulk conducting polymers, nanostructured conducting polymers are expected to exhibit improved performances in technological applications because some unique properties may arise from their nanoscale morphology [20]. Conducting polymer nanotubes and nanowires with diameters less than 100 nm can be made by hard templates such as porous polycarbonate films [21], or porous alumina [22], which usually have to be removed after synthesis of PPy nanostructures. Nevertheless, this route appears to be risky as it may damage the synthesized PPy structures due to the use of strong acid/alkaline aqueous solutions, organic solvents, or elevated temperatures. On the other hand, soft templates such as reverse microemulsions [23] or micelles [24] may have the disadvantages of instability, low efficiency, and lack of versatility.

The conducting polymers are used in different electrolytes to obtain a higher specific capacitance. For example, the best electrolytes for polyaniline are usually acidic solutions [25], whereas polypyrrole and polythiophene exhibit ideal capacitance behaviour in neutral and basic electrolytes [26]. Aqueous electrolytes are mostly composed of small inorganic anions (angström level) that can easily access the micropores and mesopores under an electric field. In this regard, aqueous electrolytes seem to be most favourable for pairing with micropores activated carbons for supercapacitors. Indeed, it was reported that after prolonged operation, supercapacitors based on activated carbons and organic electrolytes may reveal capacitance fading and resistance increase, together with microscopic phenomena such as gas evolution, increase of the electrode mass or local disbonding of the coating layer from the metallic collector [27]. There is however contributions from functional surface groups, which are in general present on activated carbons and can be charged and discharged, giving rise to a pseudocapacitance [28].

Polypyrrole and carbon materials have already been associated frequently to produce competitive composite materials for supercapacitor electrodes (see a non-exhaustive list in Table 1). Our objective was thus to benefit from a simple and efficient chemical method that was developped in our group to synthesize nanostructured PPy powders by using a manganese dioxide powder as oxidizing agent and nanostructured template in presence of pyrrole [35]. In the work reported hereafter, the PPy powder thus obtained was used as active additive in carbon/carbon supercapacitors to improve their performances. The study of the capacitive performances of added PPy to activated carbon powder was carried out by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques.

2. Experimental

2.1. Chemicals

All the solutions were prepared using deionised water with double ion exchange columns. Sulphuric acid (H_2SO_4) and ethanol (C_2H_5OH) were purchased from Prolabo. Pyrrole was purchased from Fluka (97% purity) and was purified by distillation before use. Picactif BP 10™ (hereby referred to as PICA) is commercially available activated carbon, and was used as received. Its nominal specific surface area was 2000 $m^2\ g^{-1}$. The characterization of PICA by different physical techniques was realized by different research groups [9,10,36].

2.2. Nanostructured polypyrrole powder

The chemical synthesis and the characterization of this powder has already been reported in a previous publication [35]. It consisted of a hydrothermal synthesis of MnO_2 powder [37,38] followed by the polymerization of pyrrole using MnO_2 simultaneously as oxidizing agent and template. The polypyrrole powder was chemically prepared by injecting liquid pyrrole (0.2 M) into a beaker containing MnO_2 powder (2 g) suspended in a H_2SO_4 (100 mL, 1 M) aqueous solution at room temperature. The mixture was stirred with magnetic bar for 1 h at room temperature. The black precipitate of polypyrrole was collected by filtration, rinsed repeatedly with deionised water, and finally dried at 60 °C for 24 h.

2.3. Electrochemical tests

The PICA electrode was prepared by mixing 95% (in mass) PICA and 5% PTFE into 5 mL of ethanol (95%). The PICA/PPy composite electrodes were prepared, unless described differently, by mixing 85% PICA, 10% PPy, and 5% polytetrafluoroethylene (PTFE) into 5 mL of ethanol (95%). After evaporation of ethanol, these mixtures were pressed in a roller and dried at 120 °C for 24 h. A 1.5–1.8 mm thick soft film was then obtained. A disk of 0.6 cm in diameter was then cut out by punching. The frontal surface area was thus 0.29 cm^2. The disk thus obtained weighed about 8 mg.

The electrochemical behaviour of these electrodes was evaluated using CV and EIS techniques. All electrochemical experiments were carried out by using the Swagelok-type device presented in Fig. SI-1a. Two active materials based disk electrodes were set together with a separator made of a filter paper between them as illustrated in Fig. SI-1b.

They were then inserted into a stainless-steel tube of the Swagelok-type cell. The electrical isolation of the electrodes to the cylinder was ensured by a 100 μm-PET (polyethylene terephthalate) sheet. Two cylinders push the electrodes towards the centre of the tube by means of two nuts to make electrical contact. The PET spacers set on each cylinder wall allowed the electrical isolation to the central tube. A small plug set at the extremity of each cylinder was used to connect the potentiostat.

The electrochemical tests were carried out with the help of two active material based pellets possessing close masses and separated by a filter paper impregnated with the 1 M $NaNO_3$ aqueous electrolytic solution.

The CV tests were performed in the potential window extending from −0.4 to 0.6 V (vs. open-circuit potential, E_{OC}) using a Bio-logic SP 300 potentiostat controlled by the EC-Lab V10.11 software.

The EIS measurements were performed using Dielectric interface Solartron 1296A gain phase impedance analyzer coupled with a frequency response analyser (FRA 1255B) and computer-