



ELSEVIER

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Capacitive behaviour of polypyrrole, prepared by electrochemical and chemical methods



S. Chen, I. Zhitomirsky*

Department of Materials Science and Engineering, McMaster University, 1280 Main Street West, Hamilton, ON, Canada L8S 4L7

ARTICLE INFO

Article history:

Received 7 March 2014

Accepted 21 March 2014

Available online 28 March 2014

Keywords:

Polypyrrole

Galvanostatic electropolymerization

Pulse electropolymerization

Chemical polymerization

Supercapacitor

Electrode

ABSTRACT

Polypyrrole (PPy) electrodes for electrochemical supercapacitors were prepared by galvanostatic electropolymerization, pulse electropolymerization and chemical polymerization methods using pyrocatecholsulfonphthalein as an anionic dopant. Pulse electropolymerization provided improved impregnation of Ni plaque current collectors and formation of nanostructured coatings on Ni particles. The electrodes prepared by pulse electropolymerization showed higher porosity, improved PPy contact with current collectors, higher capacitance, lower electrical resistance, improved capacitance retention at high charge–discharge rates and improved cycling stability. The use of Ni plaque current collectors allowed good electrochemical performance at high PPy mass loading. The highest capacitance of 320 F g^{-1} was achieved at a scan rate of 2 mV s^{-1} .

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Polypyrrole (PPy) is currently under intensive investigation for applications in electrodes of electrochemical supercapacitors (ES) [1]. The interest in PPy for energy storage in ES is attributed to high specific capacitance (SC) and high conductivity of this material. Previous investigations have generated significant interest in the development of PPy films on commercially important non-noble current collectors for applications in devices, based on Na_2SO_4 electrolyte [2].

PPy can be prepared by electrochemical [2] or chemical [3] polymerization methods. In the anodic electropolymerization method, the pyrrole (Py) monomer, dissolved in a solvent, containing an anionic dopant, is oxidized at the electrode surface by the applied anodic potential to form a polymer film. Chemical polymerization method allows the formation of PPy powders by the oxidation of Py monomers in the bulk solutions in the presence of oxidants and dopants. Many investigations were focused on the development of polymerization techniques for the fabrication of porous nanostructured PPy, which allows good electrolyte access to the material surface for charge-discharge reactions [4–6]. Anionic dopants showed significant influence on the microstructure and electrochemical performance of PPy, prepared by chemical and electrochemical polymerization methods [1,7,8]. A problem, limiting the use of PPy in ES is poor cycling stability.

It was found that swelling, caused by the anion exchange between PPy and electrolyte during cycling has a detrimental effect on cycling stability [1,9]. The material swelling usually results in the loss of film adhesion during cycling, increasing interface resistance and reduced capacitance. Such problems were addressed in our investigation.

The goal of this investigation was the fabrication and testing of PPy electrodes, formed by chemical and electrochemical polymerization. The approach, described below, is based on the impregnation of porous Ni-plaque current collectors with PPy. The comparison of the electrodes prepared by the different impregnation methods indicated superior electrochemical performance of the electrodes prepared by pulse electropolymerization, which showed high capacitance at relatively high materials loadings, reduced resistance, good capacitance retention at high scan rates and good cyclic stability.

2. Experimental procedures

Pyrrole (Alfa Aesar), pyrocatecholsulfonphthalein (PS) and ammonium persulfate (APS) (Aldrich) were used as starting materials. Commercial Ni plaques, designed for high power battery applications, were supplied by Vale Canada. Electropolymerization and chemical polymerization were performed using 0.1 M pyrrole solutions, containing 5 mM PS. Anodic electropolymerization was performed by galvanostatic and pulse (ON and OFF times of 0.5 s) methods at a current density of 1 mA cm^{-2} . Chemical polymerization was conducted by adding 50 mM APS as an oxidant. After stirring for 3 h, the obtained PPy was filtered, washed with

* Corresponding author. Tel.: +1 905 525 9140.

E-mail address: zhitom@mcmaster.ca (I. Zhitomirsky).

deionized water and then dried in air. PPy powder was dispersed in ethanol to prepare a slurry, which was then impregnated into Ni plaques.

Scanning electron microscopy (SEM) studies were performed using a JEOL JSM-7000F microscope. Electrochemical tests were carried out with a potentiostat (PARSTAT 2273, Princeton Applied Research) using 0.5 M Na₂SO₄ aqueous solutions. Ni plaques, impregnated with PPy, were used as working electrodes. The area of the working electrodes was 1 cm². Platinum gauze was used as counter electrode, and the reference electrode was a standard calomel electrode (SCE). Cyclic voltammetry (CV) studies were performed within a potential window (ΔV) from -0.5 to $+0.4$ V versus SCE at scan rates of 2–100 mV s⁻¹. The specific capacitance was calculated using the expression:

$$C = Q/m\Delta V$$

where Q is charge obtained by half the integrated area of the CV curve, m is the PPy mass. The measurement of electrochemical impedance was conducted within a frequency range of 10 mHz–100 kHz with AC signal amplitude of 5 mV.

3. Results and discussion

The interest in PS (Fig. S1A) as a new polyaromatic anionic dopant for PPy polymerization was based on the literature data, which indicated that PPy doped with polyaromatic dopants showed reduced particles size, high conductivity and improved electrochemical performance [1,2,7]. Preliminary experiments showed that adherent films can be obtained on Ni foil substrates by electropolymerization (Fig. S1B). The film adhesion measurement according to the ASTM D3359 standard indicated that the film strength corresponded to 4B classification for film mass of 0.1–0.3 mg cm⁻². The films showed capacitive behaviour (Fig. S2), however, the capacitance reduced by 50% after 500 cycles. The increase in the PS concentration in the range of 2.6–5.0 mM resulted in increasing capacitance and decreasing impedance, but no significant variations in capacitance and impedance was observed at higher PS concentrations (Fig. S3). The optimum amount of PS was found to be 5 mM.

Fig. 1A and B shows deposition yield as a function of deposition time for galvanostatic and pulse electropolymerization of PPy. The deposition yield increased nearly linearly with increasing deposition time. Therefore, the amount of the deposited material can be varied and controlled. Fig. 2 compares the SEM images of as-received and electrochemically impregnated Ni plaques.

The as-received plaques (Fig. 2A and B) were porous, the typical size of pores and Ni particles was in the range of 1–20 and 1–3 μ m,

respectively. The SEM image of the plaques after galvanostatic electropolymerization (Fig. 2C and D) showed that porosity was closed by the PPy material. However, the PPy layer showed cracks. It is suggested that voids in the porous plaque substrate below the PPy layer promoted crack formation. It is in this regard that cracks were not observed for galvanostatically deposited films on Ni foils (Fig. S1B). The analysis of SEM images of PPy plaques after pulse electropolymerization (Fig. 2E and F) showed that individual Ni particles were coated with PPy. The size of individual PPy particles was on the nanometric scale (Fig. 2F). Small pores of Ni plaques were closed with PPy material, whereas larger pores remained open. Such pores were beneficial for the ES electrodes, because they allowed good electrolyte access to the bulk of PPy active material. The analysis of SEM images at different magnifications for the electrodes, impregnated with chemically polymerized PPy (Fig. 3A and B), showed porous microstructures, containing PPy particles with typical size of 100–200 nm. However, such particles formed agglomerates.

Testing results showed nearly box shape CVs (Fig. 4A) for the electrodes, prepared by different methods. The electrodes, prepared by the electrochemical methods showed higher capacitance, compared to the electrodes prepared using PPy powders, prepared by chemical polymerization (Fig. 4B). Pulse electropolymerization allowed the fabrication of electrodes with higher capacitance and improved capacitance retention at high charge-discharge rates, compared to galvanostatic electropolymerization (Fig. 4B). The highest capacitance of 320 F g⁻¹ (0.64 F cm⁻²) was obtained at a scan rate of 2 mV s⁻¹ for the PPy electrodes, prepared by pulse electropolymerization. The electrodes showed capacitance retention of 58% at a scan rate of 100 mV s⁻¹. The results of impedance measurements presented in the Nyquist plot (Fig. 4C) showed that the electrodes, prepared by pulse electropolymerization exhibited lower resistance $R=Z'$, compared to the electrodes prepared using galvanostatic and chemical polymerization methods. The lower resistance can explain higher capacitance of the electrodes prepared by pulse electropolymerization. The results of impedance measurements are in good agreement with the simulation data, obtained using the equivalent circuit shown in Fig. 4C(inset). This circuit included electrolyte resistance R_1 and charge transfer resistance R_2 . Constant phase elements Q_1 and Q_2 represent pseudocapacitance and double layer capacitance, respectively. The electrodes, prepared using pulse electropolymerization showed improved cycling stability, compared to the electrodes prepared by galvanostatic electropolymerization and chemical polymerization (Fig. 4D). The increase in capacitance during the first 400 cycles (Fig. 4D(b)) can be attributed to morphological changes in PPy layers during cycling, the capacitance retention after 1000 cycles was 92%. The use of Ni plaque current collectors offered the

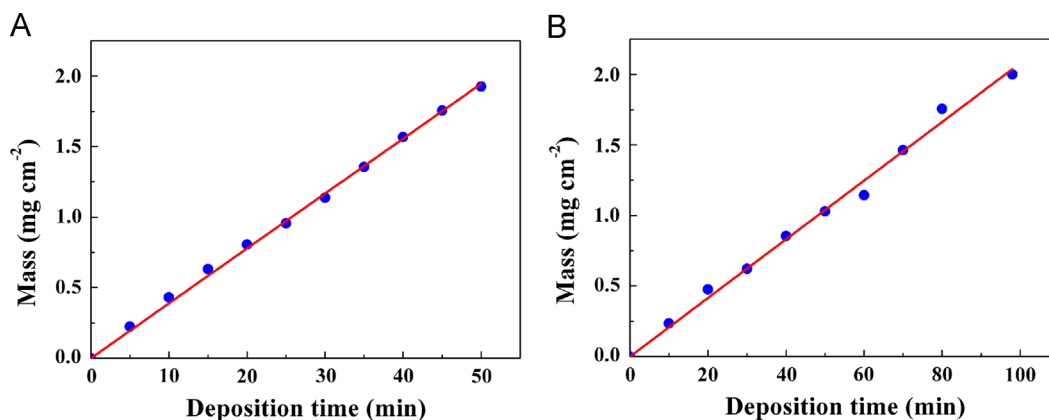


Fig. 1. Deposit mass versus deposition time for (A) galvanostatic electropolymerization and (B) pulse electropolymerization.

Download English Version:

<https://daneshyari.com/en/article/1644065>

Download Persian Version:

<https://daneshyari.com/article/1644065>

[Daneshyari.com](https://daneshyari.com)