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Electrodeposition of polypyrrole–carbon nanotube composites for electrochemical supercapacitors

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HIGHLIGHTS

- ► Composite polypyrrole–carbon nanotube films were obtained electrochemically.
- ► Pyrocatechol violet was used as anionic dopant, dispersing and charging agent.
- ► Composite films were investigated for applications in electrochemical supercapacitors.
- ► Stainless steel foils and porous nickel plaques were used as current collectors.
- ► Nickel plaques allowed higher capacitance and higher materials loading.

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ABSTRACT

In this work we introduce a new electrochemical strategy for the fabrication of composite polypyrrole (PPY)–multiwalled carbon nanotube (MWCNT) composites for electrochemical supercapacitors (ES). The problem of low adhesion of PPY films on stainless steel and Ni substrates is addressed by the use of pyrocatechol violet (PV) dye as an anionic dopant. The experimental data indicates that strong adhesion of PPY films is attributed to catecholate type of PV bonding. We also find that PV strongly adsorbs on MWCNT and allows efficient dispersion, charging and controlled electrophoretic deposition (EPD) of MWCNT. The use of PV for electropolymerization of PPY and EPD of MWCNT allows the formation of composite films by combined electrodeposition method. Results show that Ni-plaque current collectors developed for high power battery applications can be electrochemically impregnated with PPY–MWCNT to form electrodes for ES. Ni plaque based electrodes offer advantages of significantly higher materials loading and superior capacitive behavior compared to thin film electrodes formed on stainless steel current collectors. The electrodes obtained by pulse impregnation show higher specific capacitance compared to the electrodes prepared by galvanostatic impregnation.

1. Introduction

The growing interest in application of polypyrrole (PPY) for electrodes of electrochemical supercapacitors (ES) is attributed to high specific capacitance (SC), relatively large voltage window, high electrical conductivity, low cost, advanced chemical and mechanical properties of this material [1]. The high SC of PPY results from redox reactions, which allow charge storage in the bulk of the electrode material. Many fundamental investigations have been conducted with the objective to investigate the charging mechanism of PPY in different electrolytes and to utilize high theoretical SC of PPY (620 F g^{-1}) [1–4] in electrodes of ES.

The fabrication of PPY films by electropolymerization is an attractive technique that allows the pyrrole monomer, dissolved in a solvent, containing an anionic dopant, to be oxidized at the electrode surface by the applied anodic potential, forming a polymer film [5–7]. The anionic dopant is incorporated into the polymer to ensure electrical neutrality of the resulting film. Many studies were focused on modification of PPY based materials, optimization of film deposition conditions, and development of advanced anionic dopants [8–10]. Relatively high electrical conductivity and thermal stability of PPY films was achieved using aromatic anionic dopants [11–13]. It was shown that with the variation of the dopant anion, the conductivity of the PPY thin films can differ by three orders of magnitude [14]. The relatively high electrical conductivity and advanced electrochemical properties, achieved using *p*-toluenesulfonate, anthraquinone-2-sulfonate, benzenesulfonate and other dopants, resulted in intensive research

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on chemical interactions of PPY and aromatic anionic molecules [14–16]. Especially interesting are the investigations of composite materials containing carbon nanotubes in the PPY matrix [17,18]. Such composites showed reduced resistance and improved capacitive behavior. Also of great interest are the studies focused on the fabrication of PPY-metal oxide [19] and PPY-graphene [20–22] nanocomposites.

Despite the impressive progress achieved in the fabrication of PPY and composite electrodes of ES by electropolymerization, there is a need for further development of this method. One of the major challenges of electrochemical polymerization of pyrrole involves formation of adherent PPY films on non-noble metal substrates, as oxidation and dissolution of the substrates during anodic electropolymerization occurs readily. PPY based ES showed excellent capacitive behavior in H_2SO_4 [5,23] and HCl [8] electrolytes. The problems of corrosion of current collectors and chemical degradation of CNT in the acidic electrolytes can be diminished using Na_2SO_4 electrolyte [24]. However, the SC of PPY in Na_2SO_4 is usually lower, compared to that in acidic electrolytes.

PPY films were formed on low carbon steels using oxalic acid solution electrolyte [25]. It was shown that steels interacted with oxalic acid to form passive layers, which prevented corrosion of the substrates. However, the formation of the non-conductive and non-capacitive iron oxalate layer [26,27] results in increasing charge transfer resistance and reduced electrochemical capacitance of the PPY coated current collectors.

Recent studies [28] highlighted the importance of high active material loadings for the fabrication of efficient ES. However, the increase in material loading usually results in increased resistance and reduced SC. This problem can be addressed by the use of special current collectors, such as Ni foams or plaques. Previous investigations showed that Ni plaques [29], designed for high power applications, allowed significantly higher SC of MnO_2 electrodes, compared to MnO_2 electrodes based on Ni foams [30]. The advantages of Ni plaque based electrodes were especially evident at high charge–discharge rates. The important challenge is the electropolymerization of PPY on high surface area Ni plaque electrodes. Another strategy is based on the fabrication of PPY–CNT composites [17]. CNT are usually added to active materials in order to increase the electronic conductivity of the composite electrodes and improve the power density of ES. The use of CNT as conductive additives offers benefits of their high surface area and low percolation threshold. However, the specific capacitance of CNT is low. Therefore, the fabrication of PPY–CNT electrodes requires efficient dispersion of CNT in the PPY matrix and optimization of the CNT content in the composites. In order to achieve this goal, CNT must be well dispersed and negatively charged in the pyrrole solutions and incorporated into the growing PPY films. However, for CNT applications, which depend on electrical conductivity, it is challenging to achieve good dispersion, charging and controlled electrodeposition of pristine CNT and avoid defects due to chemical treatment or functionalization [17].

The goal of this investigation was the electrochemical fabrication of composite PPY–multiwalled carbon nanotubes (MWCNT) electrodes using stainless steel and Ni plaque current collectors. The approach is based on the use of organic dyes as anionic dopants for PPY electropolymerization. The comparison of the chemical structures and experimental data for pyrocatechol violet (PV) and *m*-cresol purple (CP) provided an insight into the deposition mechanism, which allowed the formation of adherent films using PV. The important finding was the possibility of efficient dispersion and controlled electrodeposition of MWCNT using PV as a dispersing agent. The results presented below showed that pulse deposition offers advantage of higher SC of Ni plaque based PPY–MWCNT composites, compared to the SC of similar electrodes prepared by the galvanostatic deposition.

2. Experimental procedures

Pyrrole, PV, CP (Aldrich), MWCNT (Arkema) were used for the fabrication of solutions and suspensions for electrodeposition. Commercial Ni plaques [31] were supplied by Vale Canada. Aqueous solutions of pyrrole, containing PV or CP were used for electropolymerization. PPY films were obtained galvanostatically at a current density of 1 mA cm^{-2} from 6.7 g L^{-1} pyrrole solutions, containing 1 g L^{-1} PV or CP. Potentiodynamic deposition of PPY films was performed at a scan rate of 20 mV s^{-1}. Electrophoretic deposition (EPD) of MWCNT was performed from aqueous suspensions, containing 0.1–1 g L^{-1} MWCNT and 0–1 g L^{-1} PV. The suspensions containing MWCNT were ultrasonicated for 30 min to achieve a homogeneous dispersion. Constant voltage EPD was performed at a deposition voltage of 20 V. Constant current EPD was performed at a current density of 1 mA cm^{-2}. Composite PPY–MWCNT deposits were obtained from aqueous 6.7 g L^{-1} pyrrole solutions, containing 0.1 g L^{-1} MWCNT and 1 g L^{-1} PV, using galvanostatic deposition or pulse deposition with ON and OFF times of 0.5 s at a current density of 1 mA cm^{-2}.

The electrodeposition cell included a substrate and Pt counter electrode. Stainless steel (grade 301) foil or Ni plaque substrates were used for deposition. The distance between the substrate and counter electrode was 15 mm. Deposition yield was studied at various PV concentrations and different deposition durations. A minimum of 3 samples were prepared in each deposition experiment. All the deposits were obtained using fresh solutions. The deposition yield measurements were repeatable and the error was less than 5%. Film adhesion was tested according to the ASTM D3359 standard.

The microstructure of the films was investigated using a JEOL JSM-7000F scanning electron microscope (SEM). Electrochemical studies were performed using a potentiostat (PARSTAT 2273, Princeton Applied Research). Surface area of the working electrode was 1 cm^2. The counter electrode was a platinum gauze, and the reference electrode was a standard calomel electrode (SCE). Capacitive behavior and electrochemical impedance of the films were investigated in 0.5 M Na_2SO_4 aqueous solutions. Cyclic voltammetry (CV) studies were performed within a potential range of −0.5 to +0.4 V versus SCE at scan rates of 2–100 mV s^{-1}. The specific capacitance (SC) was calculated using half the integrated area of the CV curve to obtain the charge (Q), and subsequently dividing the charge by the film mass (m) and width of the potential window (ΔV):

$$C = \frac{Q}{m\Delta V} \tag{1}$$

Impedance spectroscopy investigations were performed in the frequency range of 0.1 Hz–100 kHz, the amplitude of the applied voltage was 5 mV.

3. Results and discussion

Fig. 1 shows chemical structures of PV and CP molecules used in this investigation. PV and CP are polyaromatic compounds with similar structures. The anionic properties of the molecules are related to their SO_3^- groups. The structure of PV includes two OH groups bonded to the adjacent carbon atoms of the aromatic ring. PV and CP were investigated as anionic dopants for electropolymerization of PPY and as charging and dispersing agents for the electrodeposition of MWCNT.