Electrochimica Acta 147 (2014) 545–556

Contents lists available at ScienceDirect

Electrochimica Acta

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

Galvanostatic deposition of polypyrrole in the presence of tartaric acid for electrochemical supercapacitor

Erhan Karaca, Nuran Özçiçek Pekmez *, Kadir Pekmez

Hacettepe University, Department of Chemistry, 06800 Ankara, Turkey

ARTICLE INFO

Article history:
Received 14 June 2014
Received in revised form 20 August 2014
Accepted 27 September 2014
Available online 2 October 2014

Keywords:
Supercapacitor
Electrodeposition
Polypyrrole
Tartaric acid
Pencil graphite

ABSTRACT

Galvanostatic deposition of tartrate–doped polypyrrole (PPy) is carried out on platinum foil in acetonitrile solution with tartaric acid, tetrabutylammonium tetrafluoroborate and Triton-X 100 for supercapacitor studies. The effect of substrate is studied by comparing the results obtained by using platinum, stainless steel and pencil graphite electrodes. The capacitive performance of the coatings are evaluated in an H_2SO_4/water medium by cyclic voltammetry, electrochemical impedance spectroscopy and galvanostatic charge–discharge methods. Based on the charge–discharge results obtained, the tartrate–doped PPy coatings represent a high specific capacitance of 794 F g^{-1} (areal capacitance of 238 mF cm^{-2}) and a high energy density of 105 Wh kg^{-1} on pencil graphite electrode, and a high power density of 36.3 kW kg^{-1} on 316Ti stainless steel electrode. High values may be attributed to the incorporation of tartaric acid via hydrogen bonding, and/or tartrate anion as dopant together with the tetrafluoroborate anion. Besides, Triton X100 provides high porosity and therefore high surface area.

1. Introduction

Supercapacitors are being developed as an alternative to batteries and capacitors. They have much higher power density, lower energy density and longer cycle life than batteries [1]. Generally, supercapacitors can operate over a wide range of temperatures and their coulombic efficiencies are as high as 99%. The equivalent series resistance in supercapacitors is extremely low, so they can be charged with a very high current, which is not possible in energy storage devices like batteries.

Due to the pseudocapacitive properties of polyaniline, polypyrrole, polythiophene and their derivatives, they are studied as electrode materials for redox capacitors. Polypyrrole (PPy) offers a higher specific capacitance and a greater degree of flexibility in electrochemical processing than most conducting polymers, and consequently the material has been the subject of much research as a supercapacitor or battery electrode. The specific capacitance of PPy coated electrodes has been reported over a range of 179 F/g to 506 F/g at a scan rate of 10.0 mV s^{-1} [2–4]. These capacitances are much higher than those of the electrodes based on commercial activated carbons (<200 F/g at 1 mV s^{-1}) [5], but lower than those fabricated with expensive, rare metals, such as ruthenium oxide (1170 F/g at 10.0 mV s^{-1}) [6]. However, PPy could have as high specific capacitances as metal oxides when electrosynthesized in the presence of various dopants based on organic acid such as oxalic acid (480 F g^{-1} at 10 mV s^{-1} on Ti foil) [2], p–toluene sulphonic acid (200 F g^{-1} at 0.8 mA cm^{-2} on stainless steel) [7], 2,7–Bis(2–sulfophenylazo) chromotropic acid (about 200 F g^{-1} at 20 mV s^{-1} on Ni foam) [8], chromotropic acid (343 F g^{-1} at 2 mV s^{-1} on stainless steel) [9], 5–sulfosalicylic acid (545 F g^{-1} at 2 mV s^{-1} on stainless steel) [10], sulfanilic acid (5.43 F cm^{-2} at 2 mV s^{-1} on Ni foam) [11] and in the presence of various surfactants such as sodium dodecyl benzene sulfonate (95 mF cm^{-2} at 50 mV s^{-1} on Pt electrode) [12]. PPy film–coated stainless steel electrode, studied by Zhang *et. al.*, was prepared by pulse galvanostatic method in aqueous solution containing p–toluene sulphonic acid and determined as 403 F g^{-1} at 0.5 mA cm^{-2} of the specific capacitance [13]. Generally, organic acids improve the properties of conducting polymers as not only capacitance but also stability [14]. Also, surfactants provide enhancement in the specific area of coating.

Polythiophene and polyaniline were also prepared for supercapacitor studies in the presence of various organic acids [14,15] as well as cationic, anionic, non–ionic surfactants [16,17]. Gnanakan *et al.* investigated that polythiophene prepared with tartaric acid exhibited higher specific capacitance of 156 F g^{-1} at 5.00 mV s^{-1} on stainless steel [14]. Senthilkumar *et al.* studied the chemical oxidative polymerization of polythiophene in aqueous medium using such surfactants as Cetyl trimethylammonium bromide, Sodium dodecyl sulfate and Triton X100 (TX100) [16]. The polythiophene prepared with TX100 exhibited higher specific

* Corresponding author. Fax: +90 312 299 2163.
E-mail address: npekmez@hacettepe.edu.tr (N.Ö. Pekmez).

http://dx.doi.org/10.1016/j.electacta.2014.09.136
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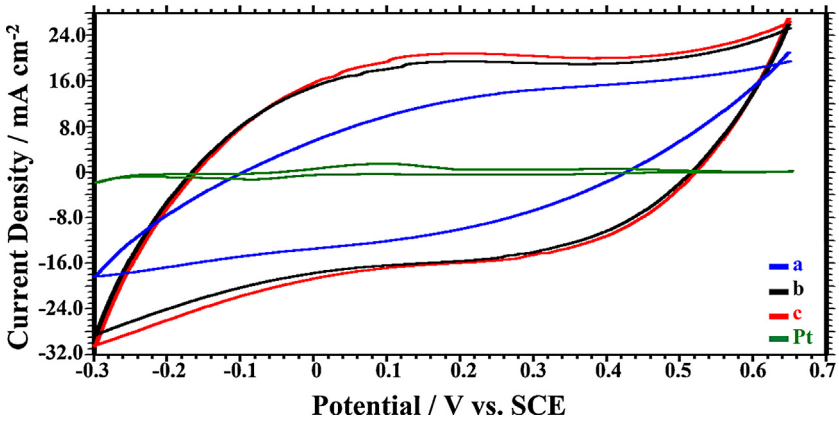

Fig. 1. Cyclic voltammograms recorded in 0.100 M H_2SO_4 solution for 0.3 mg cm^{-2} of PPy prepared on Pt electrode in an acetonitrile solution containing (a) pyrrole and $TBABF_4$ (b) pyrrole, $TBABF_4$ and TA/T^- (c) pyrrole, $TBABF_4$, TA/T^- and TX100, and (Pt) for bare Pt electrode. .$C_{pyrrole}$: 50.0 mM, C_{TBABF4}: 25.0 mM, C_{TA}: 25.0 mM, C_{TBAT}: 25.0 mM, C_{TX100}: 25.0 mM, v = 100 mV s^{-1}.

capacitance of 117 F g^{-1} compared with that of surfactant free polythiophene (78.0 F g^{-1} at 5.00 mV s^{-1}) on graphite. A similar type of enhanced specific capacitance was reported by Girija et al. [15] for the case of polyaniline when TX100 was used as the surfactant (805 F g^{-1} at 3 mA cm^{-2} on stainless steel).

Martins et al. studied the electrochemical polymerization of PPy with tartaric acid on aluminum for corrosion studies [18]. This bilayer Al_2O_3/PPy showed high corrosion resistance of 38 k Ω in 3% NaCl medium, and also high specific capacitance of 1.62 μF cm^{-2} according to synthesis conditions. There has been no report on the synthesis of PPy on platinum foil (Pt), 316Ti stainless steel (316Ti SS) and disposable pencil graphite (PG) electrodes in the presence of both tartaric acid (TA) and TX100 for supercapacitor studies. Hence, in this study, polypyrrole films are galvanostatically deposited on these electrode surfaces from acetonitrile solutions containing pyrrole as monomer, tartrate and tetrafluoroborate ions as dopant, TX100 as surfactant, applying different current density, including multi–step currents. It is expected that TA and/or T^- ions immobilize in polymer, due to the ability of construction of hydrogen bonds by–N–center in the pyrrole ring [19]. The tetraalkylammonium cation is preferred for preparing tartrate salt due to fact that the tetraalkylammonium salts promotes the formation of the hydrogen-bonded chains from the compounds that can form hydrogen bonds [20–22]. Polymerization solution is prepared by adding pyrrole, TA, TBAOH, $TBABF_4$ and TX100. TA and TBAOH are reacted to yield tetrabutylammonium tartrate (TBAT). Thus, the polymerization solution consists of pyrrole, TA + TBAT (TA/T^-), $TBABF_4$ and TX100. The obtained coatings were characterized by cyclic voltammetry and EDX methods. Their capacitive properties were investigated in aqueous H_2SO_4 solution by using cyclic voltammetry, electrochemical impedance spectroscopy (EIS) and galvanostatic charge–discharge studies.

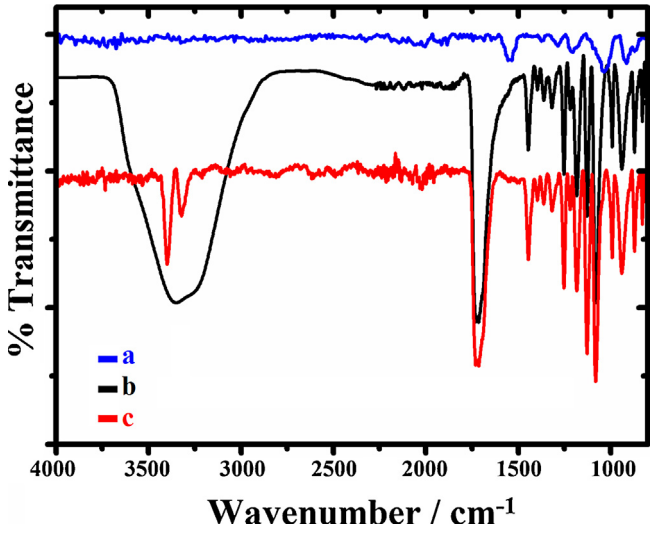

Fig. 2. FTIR spectra of PPy coatings (a) in the absence, (b) in the presence of TA and (c) pure tartaric acid.

2. Experimental

Pyrrole (Py, Fluka) was distilled under the protection of high purity nitrogen (Linde) and then kept in refrigerator before use. Triton X100 (Sigma), acetonitrile (HPLC–grade, Sigma), sulfuric acid (H_2SO_4, Fluka), dextrotartaric acid (Laboratory BDH Reagent), tetrabutylammonium hydroxide (TBAOH, Aldrich) and tetrabutylammonium tetrafluoroborate ($TBABF_4$, Aldrich) were analytical grades and were used without any further purification.

Electrochemical measurements were carried out under nitrogen atmosphere in a three–electrode type cell with separate compartments for reference electrode [Ag, AgCl (sat) in acetonitrile and saturated calomel reference electrode (SCE) in aqueous solution] and counter electrode (Pt spiral). Pt foil (0.500 cm^2) was used as working electrode. The other working electrodes were 316Ti stainless steel disc electrode (0.00785 cm^2) and pencil graphite electrode (0.015 cm^2). Geometric area of the electrode was used to calculate current density and mass of PPy per unit area [23].

The 316Ti stainless steel electrode had the following composition (wt.%): C 0.0100; Mn 1.91; Si 0.510; S 0.0300; P 0.0280; Cr 16.6; Ni 10.8; Mo 2.06; Si 0.510; Ti 0.100; Fe 68.0, respectively. The surface of stainless steel electrode was wet mechanically polished successively with 800, 1000, 1200 and 2000 abrasive paper before each electrochemical experiment. After this process, the electrode was washed with distilled water, rinsed with acetonitrile and dried at room temperature, respectively. Pencil graphite electrode is a disposable electrode. The platinum foil electrodes were cleaned by burning in a flame before each experiment. These electrodes were washed with ultra pure water and then immersed for 3 min in an acetonitrile solution. Ultimately, they were dried at room temperature. The polymer–coated electrodes were immersed in acetonitrile to remove adsorbed electrolytes, monomers and the soluble oligomers formed during electrosynthesis of the coating before studies. Then, they were dried at room temperature.

Experiments involving the deposition of polymer and its subsequent characterization by cyclic voltammetry, EIS and