Electrochimica Acta 193 (2016) 311–320

Contents lists available at ScienceDirect

Electrochimica Acta

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

Tailoring polypyrrole supercapacitive properties by intercalation of graphene oxide within the layer

D. Sačer[a], D. Čapeta[b], I. Šrut Rakić[c], R. Peter[d], M. Petravić[d], M. Kraljić Roković[a,1,*]

[a] Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, 10000 Zagreb, Croatia
[b] Faculty of science, University of Zagreb, Bijenička 32, 10000 Zagreb, Croatia
[c] Institute of Physics, Bijenička 46, 10000 Zagreb, Croatia
[d] Department of Physics and Center for Micro and Nano Sciences and Technologies, University of Rijeka, Ulica Radmile Matejčić 2, Rijeka 51000, Croatia

ARTICLE INFO

Article history:
Received 23 November 2015
Received in revised form 25 January 2016
Accepted 9 February 2016
Available online 11 February 2016

Keywords:
chronoamperometry
cyclic voltammetry
graphene oxide
polypyrrole
supercapacitors

ABSTRACT

In this work polypyrrole was prepared using different solutions of graphene oxide as the supporting electrolyte. Two different samples of graphene oxide (GO1 and GO2) were prepared from different graphite precursors. The obtained samples were characterised by means of scanning electron microscope (SEM), atomic force microscope (AFM) and X-ray photoemission spectroscopy (XPS), which showed a significant difference between the two structures considering their morphology characteristics, sheet size and type of oxygen functionalities. However, all the graphene oxide samples used in this work contain appropriate amounts of $—COO^-$ groups essential for compensation of positive charge generated at the polymer backbone.

The polymer layers were prepared by cyclic voltammetry and chronoamperometry methods from GO1 (PPy/GO1), GO2 (PPy/GO2) and dialysed GO2 (PPy/D-GO2) supporting electrolyte solutions. The examinations were carried out in appropriate graphene oxide or Na_2SO_4 solutions. The results obtained reveal that the layers are electrochemically active in graphene oxide solution. However, the polymer response is significantly improved in Na_2SO_4 solution. Electrochemical quartz crystal nanobalance (EQCN) measurements suggest that graphene oxide is involved in the polypyrrole redox reaction while the morphology characteristics suggest that graphene oxide is incorporated within the polymer layer. The properties of the layer depend on the type of graphene oxide solution used during the synthesis. The specific capacitance value of the PPy/D-GO2 layer prepared by the chronoamperometry method was found to be dependent on the deposited material mass and for 1.20 to 0.38 μg of polypyrrole it ranged between 149.51 and 221.76 F g^{-1}, respectively.

1. Introduction

Conductive polymers are interesting due to advantages such as low price, the simple method of preparation, low weight and quite fast redox reaction. Their specific processes like counter-ion intercalation, colour change and redox reaction in a wide potential range allow their application for sensors, drug release, electrochromic devices and energy power sources. Conductive polymers are especially interesting as active material in supercapacitors due to the fast redox reaction and electrochemical activity in wide potential range. Good ionic and electronic conductivities are essential for a good electrochemical activity of conductive polymer and the usage of such material in supercapacitors. In order to improve their properties, composites of conductive polymers and other materials like metal oxide [1–4] or carbon material [5–11] have been used. Carbon materials can improve the electrical conductivity as well as the porosity of the material which facilitates the overall redox reaction process.

Graphene oxide (GO) is a soluble form of graphene which is not conductive due to the presence of defects within the structure, i.e., due to the presence of different oxygen groups and the high degree of sp^3 hybridisation. These groups contribute to high solubility, increased material resistance as well as to the anionic character of the material.

GO's negative surface charge can be utilised for compensation of the positive charge generated at the oxidised polymer backbone. The conductive polymer charge is usually compensated using small-size inorganic anions or slightly larger dodecyl-sulfate, and

---

* Corresponding author. Tel.: +385 1 4597112.
E-mail addresses: dsacer@fkit.hr (D. Sačer), davor_capeta@yahoo.com (D. Čapeta), isrut@ifs.hr (I. Šrut Rakić), rpeter@phy.uniri.hr (R. Peter), mpetravic@phy.uniri.hr (M. Petravić), mkralj@fkit.hr (M. Kraljić Roković).

[1] ISE member.

http://dx.doi.org/10.1016/j.electacta.2016.02.055

polystyrene sulfonate anions [12]. There are a few reports on PPy/GO composite preparation by chemical or electrochemical methods. In chemical polymerisation, oxidants are introduced into pyrrole/GO solution and therefore, besides GO, different ionic species can be intercalated within the final polymer product [13–16], which makes it difficult to estimate if GO is incorporated as a counter-ion. Konwer *et al.* [13] prepared PPy in the presence of GO by the addition of $FeCl_3$ oxidant and thus, during the oxidation process, GO or Cl^- intercalation within the PPy layer was expected. Modification of the polypyrrole layer by GO resulted in a specific capacitance value of 421 $F\,g^{-1}$. H. Xie *et al.* [15] prepared (PPy nanowires)/GO composite with a specific capacitance from 710 to 423 $F\,g^{-1}$ by using GO/cetyltrimethylammonium bromide suspension, oxalic acid as dopant and ammonium persulfate as oxidant. Such high capacitance values can be explained by polypyrrole nanowires formation. Furthermore, it seems that GO used in this work was significantly reduced that is evident from specific capacitance value of GO which is 50 $F\,g^{-1}$. It is hard to expect this capacitance value since the conductivity of GO is few orders of magnitude lower compared to reduced GO [17]. Therefore, the presence of reduced GO can additionally explain high specific capacitance values. This ambiguities suggests that it is necessary to carry out detail analysis of GO prior to use it in polypyrrole synthesis.

In the case of electrochemical preparation of PPy/GO, it is possible to use only GO solution as the supporting electrolyte [18–20] or polymerisation can be carried out in the presence of GO and other ionic species in order to increase the conductivity of the solution [21,22]. Lim *et al.* [21] successfully prepared polymer layer in the presence of GO and sodium *p*-toluene sulfonate at constant potential. GO supporting electrolyte has mostly been used as non-dialysed solutions [18,19], where traces of salts and low molecular products are present within the solution, which may affect the polymerisation process. The specific capacitance value of PPy/GO composite obtained by electrochemical polymerisation from non-dialysed GO solutions was 289 $F\,g^{-1}$ [18]. Österholm *et al.* [20] successfully prepared PPy and PEDOT layers from dialysed GO solution by applying constant potential. In this work, polymer morphology was changed and good electrochemical reversibility was achieved. The presence of GO within the polypyrrole layer was proved by X-ray photoemission spectroscopy (XPS) and scanning electron microscopy (SEM) methods. A high concentration of GO, 4.4 mg/mL, was used in order to obtain good conductivity of the dialysed GO solution. The authors did not specify a specific capacitance value of PPy/GO layer.

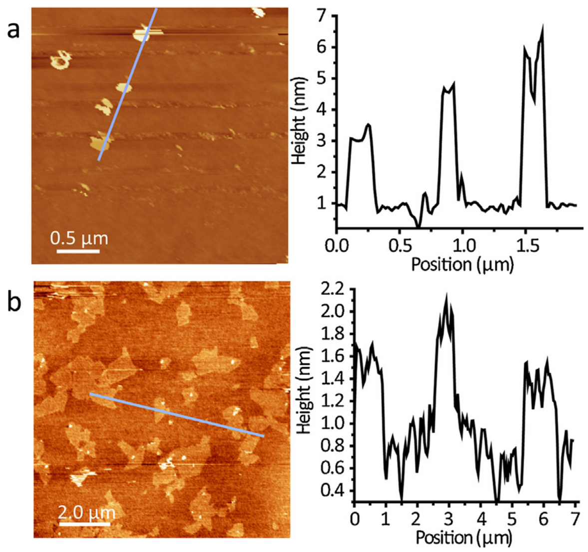

Fig. 1. AFM topography image of a) GO1 and b) GO2 sheets. Figures on the right present a line scan taken across the blue line marked on the corresponding topography image.

The aim of this work was electrochemical synthesis of PPy in the presence of GO (PPy/GO) without any additional dopant in order to incorporate GO as counter-ion within polypyrrole layer. By using this procedure GO is expected to be homogeneously dispersed within the polymer layer and thereby significant porosity of the material is expected. The high degree of porosity facilitates the ion exchange process and improves the reversibility of redox reaction. In this work different GO solutions were used as supporting electrolyte during the synthesis in order to determine the influence of the GO structure on the polymerisation process. For the first time we report results on the synthesis from dialysed GO solution with a two Pt-electrode system where reference electrode was not used in order to avoid the presence of any ionic species. PPy/GO layers were characterised using cyclic voltammetry, electrochemical quartz crystal nanobalance (EQCN) measurements and SEM.

2. Experimental

2.1. GO synthesis

Graphite oxide was prepared and purified according to Hofmann's method [23]. Nitric acid 9 mL (65%) and sulfuric acid 17.5 mL (95–98%) were added and mixed in a reaction flask using a magnetic stirring bar. The flask containing the mixture was added into an ice bath and cooled down to temperatures between 0–5 °C. Graphite 1 g (natural flakes-Sigma Aldrich or powdered graphite rod) was then added to the mixture under vigorous stirring to obtain homogeneous dispersion. While keeping the reaction flask at temperatures lower than 5 °C in the ice bath, potassium chlorate 11 g was slowly added to the mixture over 30 minutes to avoid increase in temperature. After complete dissolution of the potassium chlorate, the reaction flask was capped to avoid gas leakage and the mixture was vigorously stirred for 96 hours at room temperature. The product of oxidation, graphite oxide, was poured into the redistilled water (1 dm^{-3}), filtered, redispersed and washed repeatedly with HCl solution (5%). Afterward, it was washed with redistilled water until a neutral pH of the filtrate was obtained.

Graphene oxide suspension was prepared by ultrasonication of the graphite oxide in deionised water (40 kHz) for 2 hours and centrifuged at 4000 rpm to remove any non-exfoliated graphite oxide particles. Two different products were obtained depending on the precursor. GO1 solution was obtained using milled graphite rod precursor while GO2 solution was obtained using natural graphite flakes. The concentration of GO1 was 4 mg/mL ($pH = 2.5$ and $\kappa = 4.8\,mS\,cm^{-1}$) and for GO2 was 0.4 mg/mL ($pH = 4.0$ and $\kappa = 0.1\,mS\,cm^{-1}$). In order to remove any other residual ions generated during the oxidation step, part of the GO2 solution was dialysed for one week using Spectra/Por 4 dialysis tubing. During the dialysis process the pH value of the GO2 increased to $pH = 4.7$ and the conductivity decreased to $\kappa = 0.034\,mS\,cm^{-1}$.

2.2. XPS measurements

The XPS spectra were measured with a SPECS XPS instrument equipped with the Phoibos MCD 100 electron analyser and a monochromatized source of Al Kα X-rays of 1486.74 eV. The typical pressure in the UHV chamber during measurements was in the 10^{-7} Pa range. For the pass energy of 10 eV used in the present study, the overall energy resolution was around 0.8 eV. The