Electrochimica Acta 157 (2015) 88–94

Contents lists available at ScienceDirect

Electrochimica Acta

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

# Performance of Flexible and Binderless Polypyrrole/Graphene Oxide/Zinc Oxide Supercapacitor Electrode in a Symmetrical Two-Electrode Configuration

W.K. Chee [a], H.N. Lim [a,b,*], I. Harrison [c], K.F. Chong [d], Z. Zainal [a], C.H. Ng [a], N.M. Huang [e]

[a] Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
[b] Functional Device Laboratory, Institute of Advanced Technology, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
[c] Faculty of Engineering, The University of Nottingham Malaysia Campus, Jalan Broga, 43500 Semenyih, Selangor, Malaysia
[d] Faculty of Industrial Sciences & Technology, Universiti Malaysia Pahang, 26300 Gambang, Kuantan, Pahang, Malaysia
[e] Low Dimension Materials Research Centre, Department of Physics, Faculty of Science, University of Malaya, Kuala Lumpur 50603, Malaysia

## ARTICLE INFO

*Article history:*
Received 29 October 2014
Received in revised form 17 January 2015
Accepted 18 January 2015
Available online 20 January 2015

*Keywords:*
Supercapacitor electrode
Zinc oxide
Graphene oxide
Polypyrrole
Binderless

## ABSTRACT

A fast and facile approach based on potentiostatic electrochemical polymerization was used to prepare a polypyrrole/graphene oxide/zinc oxide (PPy/GO/ZnO) nanocomposite deposited on a flexible nickel foam. Fourier transform infrared spectroscopy and energy dispersive X-ray spectroscopy revealed the presence of zinc oxide on the PPy/GO/ZnO nanocomposite. A supercapacitor was fabricated by sandwiching a filter paper immersed in a sodium sulfate solution between two nickel foam electrodes coated with the PPy/GO/ZnO nanocomposite. The electrochemical performance of the supercapacitor was characterized using a two-electrode configuration, and the cyclic voltammetry curve recorded at a fast scan rate of 100 mV/s was pseudo-rectangular. A specific capacitance of 94.6 F/g at a current density of 1 A/g was obtained from constant current charge/discharge measurements. The utilization of the pseudo-capacitive behavior of the polypyrrole and zinc oxide, and the electrical double layer capacitance of the graphene oxide, gave rise to a high energy and power density of 10.65 Wh/kg and 258.26 W/kg at 1 A/g, respectively. The capacitance of the supercapacitor after 1000 galvanostatic charge/discharge cycles was 74% of its original value. The potential application of the as-fabricated supercapacitor in realistic energy delivery systems was demonstrated by its ability to light up a light emitting diode for about 2 minutes after being charged for approximately 30 seconds.

## 1. Introduction

The increase in carbon dioxide in the atmosphere and its detrimental effects on the climate, coupled with the environmental impact of the heavy metals used in older electronic equipment, has resulted in a growing interest in the development of low-production cost energy storage devices that use environmentally benign materials [1]. Supercapacitors have recently received a great deal of attention because of their high energy density, good cycle stability, and power handling performance [2,3]. Generally, supercapacitors are classified into two types: pseudo-capacitors and electrical double layer capacitors (EDLC). The mechanism of a pseudo-capacitor involves faradaic charging/discharging between the electrolyte and electrode. In an EDLC, the charge is stored at the surface of the active material by means of the absorption/desorption of ions to form electrical double layers [4,5]. Therefore, the electrode/electrolyte interface charging mechanism has excellent stability because the reaction mainly occurs within the electrode interfaces.

The electrodes of a pseudo-capacitor are usually formed using metal oxides and conductive polymers. The multiple stable valance states of metal oxides, especially transition metal oxides, means there are a significant number of redox reactions, which results in a higher energy density compared to EDLC-based electrodes [6]. Moreover, transition metal oxides are abundant in nature and so are readily available and relatively cheap. There are, however, drawbacks to using electrodes based on metal oxides. They have a low cycling stability, which is attributed to the redox reactions not being fully reversible, along with poor electrical conductivity. Most transition metal oxides belong to a class of semiconductors that

---

* Corresponding author.
*E-mail address:* janet_limhn@yahoo.com (H.N. Lim).

http://dx.doi.org/10.1016/j.electacta.2015.01.080
0013-4686/

have a wide band gap energy [4], which results in low electron and hole concentrations, causing a low conductivity. Conductive polymers solve the low-conductivity problem of the electrode material while retaining the advantage of storing a charge via rapid faradic charge transfer. However, conductive polymers also have problems because they are generally brittle, with low mechanical strengths [7], and consequently have a poor charge/discharge cycling stability caused by mechanical damage to the electrode material as an effect of the continuous influx and outflow of electrolyte ions [8].

The cyclic stability and good electrical conductivity of EDLC materials such as carbon nanotubes and activated carbon (ActC) have prompted significant interest in these devices. However, the applications of these materials are limited by their capacitance values [9]. Meanwhile, graphene consisting of $sp^2$-hybridized carbon atoms in a two-dimensional honeycomb structure [10] has excellent electrical and mechanical properties [11]. The zero energy band gap and electron mobility of approximately 15,000 $cm^2 V^{-1}$ produce a high conductivity. This high conductivity, coupled with a superb mechanical strength of 1.0 TPa, Young's modulus of 130 GPa, and theoretical specific surface area of 2620 $m^2 g^{-1}$, suggest the use of graphene in future electronic devices [12].

In this study, a benign single-step electrochemical polymerization was used to synthesize a polypyrrole/graphene oxide/zinc oxide nanocomposite. The properties of this nanocomposite should combine the benefits of the pseudo-capacitance arising from the inclusion of ZnO and the EDLC formed at the surface of the graphene. To characterize the electrochemical performance of the nanocomposite, a simple two-electrode electrochemical cell was constructed using the nanocomposite as the electrodes. A nickel foam was used as a deposition substrate to provide mechanical strength and act as a current collector. The electrodes were separated by a dielectric filter membrane saturated with a sodium sulfate solution, which acted as both a porous ion separator and electrolyte reservoir.

## 2. Materials and methods

### 2.1. Materials

Graphite powder was obtained from Ashbury Graphite Mills Inc (code no. 3061), United States. Sulfuric acid ($H_2SO_4$, 95%–98%), phosphoric acid ($H_3PO_4$, 85%), charcoal activated powder (ChemPur), potassium permanganate ($KMnO_4$, 99.9%), hydrogen peroxide ($H_2O_2$, 30%), and hydrochloric acid (HCl, 37%) were purchased from Systerm, Malaysia. Sodium p-toluenesulfonate (NapTS), zinc sulfate heptahydrate ($ZnSO_4.7H_2O$), and sodium sulfate ($Na_2SO_4$) were provided by Merck, Malaysia. Pyrrole (99%) was purchased from Acros Organic, New Jersey, USA stored at 0 °C, and distilled before use. Nickel foam was purchased from Goodfellow Cambridge Ltd UK. Nylon membrane filter was obtained from Membrane Solutions, LLC, USA.

### 2.2. Synthesis of graphene oxide (GO)

GO was synthesized via a modified Hummer's method [13], where 3 g of graphite flakes was oxidized by the addition of an acid mixture of $H_2SO_4$:$H_3PO_4$ (9:1) and 18 g of $KMnO_4$. The mixture was stirred continuously for about 5 min to complete the oxidation process. $H_2O_2$ solution was added to stop the oxidation process, at which time the color of the solution changed from dark brown to milky yellow. The mixture obtained was then washed with a 1 M HCl solution, using a centrifuge, followed by repeated washing with de-ionized water until a constant pH of 4–5 was obtained. After washing, the graphite oxide experienced exfoliation, forming a GO gel. The concentration of GO was 5.50 mg/ml.

### 2.3. Preparation of PPy/GO/ZnO on nickel foam

A PPy/GO/ZnO nanocomposite was electro-potentiostatically deposited on the nickel foam from an aqueous solution. The aqueous solution contained 0.1 $moll^{-1}$ of PPy, 0.1 $moll^{-1}$ of NapTS as a supporting electrolyte, 1 mg/ml of GO, and 0.1 $moll^{-1}$ of $ZnSO_4$. A potentiostat–galvanostat (AUTOLAB Metrohm PGSTAT204) was used for the electrodeposition, in which the nickel foam was the working electrode, a platinum rod was used as the counter electrode, and a saturated calomel electrode (SCE) was the reference electrode. The electrochemical deposition was carried out at a constant potential of +0.8 V (E versus SCE) at ambient temperature for 15 min. PPy and PPy/GO were also prepared for comparison with PPy/GO/ZnO. An ActC electrode, formed by soaking the nickel foam in a slurry containing ActC powder and de-ionized water for 30 min and left to dry under ambient conditions, was prepared as a positive control.

### 2.4. Material characterizations

The surface morphologies of the nanocomposites were analyzed using a field emission scanning electron microscope (FEI Quanta SEM Model 400 F) equipped with an energy dispersive X-ray (EDX) feature. The Fourier transform infrared spectroscopy (FT-IR) spectra of the samples were recorded using the attenuated total reflectance (ATR) on a Fourier transform infrared spectrophotometer (Perkin Elmer 1650). The spectra were recorded over the range of 280–4000 $cm^{-1}$.

### 2.5. Preparation of supercapacitor

The as-prepared nanocomposite deposited on the nickel foam was used as the electrodes in a supercapacitor. Two identical electrodes were separated by a piece of filter paper soaked overnight in 1 $moll^{-1}$ of a $Na_2SO_4$ solution prior to use. The electrode configuration was placed securely into a Swagelok cell and subjected to electrochemical characterizations using a two-electrode configuration.

### 2.6. Electrochemical characterization

The electrochemical properties of the prepared nanocomposites were characterized using the same potentiostat–galvanostat apparatus used in the deposition of the samples. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge/discharge measurements were carried out using a two-electrode configuration. CV was perform at a working potential of −0.2 V to +0.7 V with scan rates between 2 mV/s and 100 mV/s. EIS was performed from 5 mHz to 100 kHz, with an AC amplitude of 5 mV. Galvanostatic charge/discharge cycling of the two-electrode system was carried out from 0 V to 0.9 V, and the specific capacitance ($C_m$) was calculated from the discharge curve using Eq. (1) [14,15], where $I$ is the applied current, and $dV/dt$ is the slope of the discharge curve (V/s).

$$\text{Specific Capacitance}(\mathrm{F/g}) = \frac{I}{-\mathrm{dv/dt}} \tag{1}$$

The energy density (E) and power density (P) of the electrochemical cell were calculated from the charge/discharge profiles using Eq. (2) [16,17]: