Electrochimica Acta 259 (2018) 466–473

Contents lists available at ScienceDirect

Electrochimica Acta

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

Enhancement of electrochemical performance based on symmetrical poly-(3,4-ethylenedioxythiophene) coated polyvinyl alcohol/graphene oxide/manganese oxide microfiber for supercapacitor

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ARTICLE INFO

Article history:
Received 10 October 2017
Received in revised form
25 October 2017
Accepted 1 November 2017

Keywords:
Microfiber
Graphene oxide
Manganese oxide
Polyvinyl alcohol
Poly(3,4-ethylenedioxythiophene)
Supercapacitor

ABSTRACT

In this study, a symmetrical poly (3, 4-ethylenedioxythiophene) (PEDOT) coated on poly (vinyl alcohol) (PVA)-graphene oxide (GO)-manganese oxide (MnO_2) microfibers (PVA-GO-MnO_2/PEDOT) supercapacitor was successfully prepared using a combination of two facile techniques; electrospinning and electropolymerisation. The FESEM analysis revealed the uniform distribution of manganese oxide nanoparticles on the surface of cross-linking PVA-GO microfibers and a cauliflower-like morphology was observed upon deposition of PEDOT on the surface of PVA-GO-MnO_2 microfibers. The chemical composition of PVA-GO-MnO_2/PEDOT and oxidation state of manganese were characterised using Raman and X-Ray photoelectron spectroscopies. The inclusion of MnO_2 and PEDOT in the microcomposite proved the enhancement of specific capacitance where PVA-GO-MnO_2/PEDOT exhibited a specific capacitance of 144.66 F/g compared to PVA-MnO_2/PEDOT (107.22 F/g), PVA-GO/PEDOT (94.73 F/g) and PEDOT (62.86 F/g). A wide potential window (1.8 V) was achieved for PVA-GO-MnO_2/PEDOT with an excellent capacitance retention of 91.18% suggesting an ideal capacitive behaviour and good cycling stability. PVA-GO-MnO_2/PEDOT microcomposite also showed an improved specific energy and specific power with small equivalent series resistance (34.5 Ω) and charge transfer resistance (0.62 Ω). This demonstrated that symmetric electrode of PVA-GO-MnO_2/PEDOT can offer a great promise in producing high-performance supercapacitors.

1. Introduction

Electrochemical supercapacitors have been widely known as promising energy storage devices in current and future technology compared with other electronic devices as they possess some attractive features such as long cycle life, high power density and fast charging-discharging [1–3]. In general, supercapacitors are classified into two types of charge mechanisms; electrical double layer capacitors (EDLC) and pseudocapacitors. Electrical double layer capacitors (EDLC) undergo non-faradaic charge separation for electrical energy storage. Carbon-based materials such as graphene, graphene oxide and carbon nanotube are examples of electrode materials that commonly used in EDLC which display high specific power, but relatively low in specific capacitance and specific energy [4]. Pseudocapacitors are called as redox capacitor due to their fast and reversible redox reaction occurs at active electrode/electrolyte interface. In term of specific capacitance, pseudocapacitor materials such as conducting polymers and metal oxides are relatively higher than EDLC, which make these materials to be a great demand in supercapacitor applications recently [5]. However, pseudocapacitor suffers from poor cycling stability (conducting polymer) and low conductivity (transition metal oxides). Therefore, the development of hybrid materials with a combination of EDLC and pseudocapacitor materials has been explored [6]. Hybrid supercapacitors have unique properties which they can enhance the specific energy resulted from a high specific capacitance, while increasing the specific power due to rapid charging/discharging process [7]. Transition metal oxides are commonly used in energy storage applications as they can contribute to large specific capacitance and rapid redox process [8]. There are various species of redox-active-transition metal oxides which have been utilised as pseudo-

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https://doi.org/10.1016/j.electacta.2017.11.005
0013-4686/

capacitive electrode material such as RuO_2 [9], MnO_2 [10], Co_3O_4 [11], and Fe_2O_3 [12]. Among them, MnO_2 has been recognised as an ideal transition metal oxide owing its theoretical high specific capacitance and specific energy, environmental friendly, economical and naturally abundance [13]. Unfortunately, due to the low conductivity properties of MnO_2 (10^{-5} ~ 10^{-6} S cm^{-1}), this can lead to the limitation of specific capacitance and cycling stability [14].

Graphene oxide (GO) is a derivative of graphene containing a plenty of oxygenated functional groups (hydroxyl, epoxide, carboxyl, carbonyl) which responsible to provide a large accessible surface area for charge accumulation, especially in microfiber production. In addition, the presence of functional groups in GO allows a better solubility in solvents while supplying various purposes in GO-based hybrid nanocomposite [15]. Poly (3,4-ethylenedioxythiophene) (PEDOT) is a conducting polymer that becomes the most appealing material due to its beneficial characteristics such as good electrical conductivity, rapid doping/dedoping process, chemical stability and environmental friendliness [16,17]. Although PEDOT has several advantages for achieving a good performance in a supercapacitor, it has a limitation of cycling stability due to swelling and shrinkage during charging-discharging that cause degradation of the electrode [15].

Electrospinning is a facile and versatile technique which mainly used to produce continuous fibers with a diameter ranging from micrometer to nanometer scales. Polyvinyl alcohol (PVA) is one of the biodegradable organic polymers that commonly employed in microfiber manufacture due to its superior physical and mechanical characteristics, and chemical resistance for other industrial applications [18]. Furthermore, the presence of polar hydroxyl (-OH) groups in PVA structure makes them easily to interact with some organic and inorganic materials via chemical and physical reaction [19]. Electrospun fiber shows some interesting properties such as extensive length, small diameter and pores and high surface area per unit volume which can allow them to access in any electrolytes [20]. Carbon nanofiber (CNF) decorated with MnO_2 nanowhiskers [21] and CNF/GO/MnO_2 [22] hybrid electrodes exhibited 92% and 87% capacitance retention, respectively. Herein, we report a fabricated symmetric supercapacitor of PEDOT film embedded on PVA-GO-MnO_2 microfiber which has been prepared by two facile and cost effective techniques; electrospinning and electropolymerisation. MnO_2 was introduced in the preparation of the electrospun solution and PEDOT film was electropolymerised on the surface of PVA-GO-MnO_2 microfibers. The incorporation of PVA, GO, MnO_2 and PEDOT in the microcomposite enhance the specific capacitance, conductivity, cycling stability and accessible surface area. The as prepared PVA-GO-MnO_2/PEDOT microcomposite was characterised using Field emission scanning electron spectroscopy (FESEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Materials

ITO glasses (7 Ω/sq) were procured from Xin Yan Technology Limited. Graphene oxide (GO) was obtained from Graphenea. Silver (Ag) wire (diam. 0.5 mm), polyvinyl alcohol (PVA) (Mw 89,000–98,000), 3, 4-ethylenedioxythiophene (EDOT) monomer, manganese (II) sulfate monohydrate ($MnSO_4 \cdot H_2O$) and lithium perchlorate ($LiClO_4$) were purchased from Sigma-Aldrich. Ethanol and acetone were provided by HmbG Chemicals and System, respectively. Acetonitrile and hydrochloric acid (HCl) were supplied by J.T Baker. Potassium chloride (KCl) was obtained from Fisher Scientific UK. All chemicals were directly used as received without further purification. Deionised water (18.2 MΩ cm) was utilised throughout the experiments.

2.2. Fabrication of PVA-GO-MnO_2 microfiber via electrospinning

ITO glass was subsequently degreased with acetone, ethanol and deionised water, respectively for 15 min in an ultrasonic bath. A homogenous electrospun solution was initially prepared by dispersing PVA powder (10 wt%) and 0.05 mol L^{-1} $MnSO_4 \cdot H_2O$ in deionised water. The solution was stirred at 80 °C until a homogenous electrospun solution was obtained. An appropriate amount of GO solution (0.5 mg/mL) was then added and dispersed in the solution for another 2 h another to ensure the GO was well-mixed with PVA and MnO_2. The electrospinning setup comprises of a syringe pump, a high-voltage power supply and a collector. The high voltage power supply was utilised to generate potential difference and connected to the positively charged capillary and the negative electrode was connected to the sample collector. PVA-GO-MnO_2 electrospun solution was fed in 5 mL syringe and held horizontally on syringe pump. The ITO glasses were attached on the collector that covered with aluminium foil. The electrospinning process was carried out by applying a voltage of 15 kV. The tip-to-collector distance was set to 15 cm and the flow rate was 1.2 mL/h.

2.3. Electrodeposition of PEDOT on PVA-GO-MnO_2 microfiber

The electrochemical polymerisation of PEDOT film on the surface of PVA-GO-MnO_2 microfiber was performed using a three-electrode configuration. ITO glass covered with PVA-GO-MnO_2 microfiber, silver wire coated with silver chloride and Pt wire (1 cm^2) were used as a working, pseudo reference and counter electrode, respectively. The deposition solution consisted of 0.01 mol L^{-1} EDOT and 0.1 mol L^{-1} $LiClO_4$ in acetonitrile. The PEDOT film was electrodeposited onto ITO glass at a constant potential of 1.1 V (Fig. 1) at 15 min using potentiostat (Autolab 101) connected to a computer that equipped with Nova 1.10 software.

2.4. Material characterisations

The surface morphology of PVA-GO-MnO_2/PEDOT microcomposite was investigated using field emission scanning electron microscopy (FESEM, JEOL JSM-7600F). Field transform infrared (FTIR) spectra were acquired using a Perkin Elmer Spectrum 100 in the 280–4000 cm^{-1} range. Raman spectra were recorded using Alpha 300R instrument at room temperature which equipped with a 532 nm Ar-ion laser. X-ray photoelectron spectroscopy (XPS XSAM HS Kratos Analytical) analysis was performed to identify the surface species and its chemical states.

2.5. Electrochemical measurements

All the electrochemical measurements including cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), electrochemical impedance spectra (EIS) and cycling stability were analysed using potentiostat (Autolab M101). The two-electrode cell of PVA-GO-MnO_2/PEDOT was configured, with a filter paper soaked in 1.0 M KCl was placed between them which acted as a separator. CV was performed between 0 and 1.0 V with various scan rates of 5–200 mV/s. The GCD was measured from the current density of 0.5 A/g to 4.0 A/g. Nyquist plots from EIS measurement were obtained in the range of frequency between 0.1 Hz and 100 kHz at AC amplitude of 5 mV. Cycling stability of PVA-GO-MnO_2/PEDOT microcomposite was examined for 1000 CV cycles with a 100 mV/s scan rate.