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Conducting polymer based manganese dioxide nanocomposite as supercapacitor

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ABSTRACT

Poly 3,4-ethylenedioxythiophene (PEDOT)- and polyaniline (PANI) nanocomposites were synthesized based on manganese dioxide in the form of Nanorod. Suitability of these composites was studied extensively as an electrode material for symmetric supercapacitor in a widened operating voltage window of 1.2 V. Role of manganese dioxide during reverse microemulsion polymerization in n-hexane medium for PEDOT and aqueous dispersion polymerization for PANI, have been accounted through X-ray photoelectron spectroscopy (XPS). Structural morphology as well as thermal characterization was carried out using XRD, SEM, TEM, IR and TGA. Charge storage mechanism in these nanocomposites have been investigated through cyclic voltammetry (CV) at different scan rates (2–20 mV/s), where intercalation of metal ion during reduction and de-intercalation upon oxidation predominate over surface adsorption and desorption of metal ions into electrode material. Higher specific capacitance for PEDOT–MnO_2 (315 F/g) and PANI–MnO_2 (221 F/g) are observed in comparison with its constituent MnO_2 (158 F/g) where the internal pore volume plays a significant role over the total surface area. AC impedance measurement in the frequency range 10 kHz to 10 mHz with potential amplitude of 5 mV were carried out to ascertain the pseudocapacitance (C_{FS}) arising from the redox reactions over the electrical double layer capacitance (C_{DL}) in the composite materials.

1. Introduction

Supercapacitor or electrochemical capacitor (EC) is a promising candidate for new energy device to provide high power and long cycle life, which finds application in areas such as hybrid electric vehicles, uninterrupted power supplies, etc. [1].

The operating voltage window of an EC is a critical parameter because the energy density stored in a capacitor is proportional to the square of the operating voltage window. But the operating voltage range in the case of aqueous EC is quite low (<1.0 V) due not only to electrolysis of the electrolyte (i.e. water), but also to electrochemical instability of the electrode material in aqueous medium [2]. Amorphous MnO_2 is a suitable candidate for the electrode material for pseudocapacitors because of their large capacitance and fast redox kinetics.

It possesses the advantages of low cost, sufficiently high specific capacitance, and environment-friendly nature [2–13]. Unfortunately, the voltage window of symmetric MnO_2 supercapacitor in aqueous medium has typically been limited to 1.0 V [2]. Under negative polarization in aqueous medium, MnO_2 electrode suffers from capacitance fading due to either formation of inactive Mn(II) surface species or dissolution of partially reduced MnO_2 via disproportionation reaction to Mn(III) oxide or oxy-hydroxide species, whereas, above 1.0 V under positive polarization, extensive oxidation causes electrode passivation which leads to capacitance reduction [2,14]. Moreover, intrinsically poor electronic conductivity of manganese dioxide limits its practical capacitance value to a very low level [15].

In order to improve the electrochemical performance of MnO_2, a lot of effort has been made in the fabrication of composite materials using noble metals at the expense of high cost [16,17]. On the other hand, composite materials based on conducting polymer to improve the conductivity of manganese dioxide (MnO_2) has attracted much attention because of high conductivity, good stability and excellent capacitive behaviour with high mechanical flexibility [18–20]. Moreover, electronically conducting polymers (ECPs) have an advantage over the other polymers as they have both electrochemical double layer capacitance as well as pseudocapacitance arising due to fast and reversible redox process related to π-conjugated polymer chain [21–23]. Among various conducting polymers, poly 3,4-ethylene dioxythiophene (PEDOT) and polyaniline (PANI) have been extensively studied due to their

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controllable electrical conductivity and environmental stability. However, PEDOT and PANI like other ECPs also suffer a serious problem of typical volumetric swelling and shrinking during the insertion and ejection of counter ions [24–28]. Development of coaxial MnO_2/PEDOT nanowires based on anodic anodised alumina (AAO) [29,18,19], electrochemically fabricated MnO_x/PEDOT electrode materials in hot condition [20], a unique hierarchical MnO_2 architecture grown on functionalized carbon nanotube followed by PEDOT–PSS polymerization based ternary composite [30], etc. exhibit excellent electrochemical capacitance, but the critical experimental condition employed in the synthesis (viz. using brittle templates, imposing harsh experimental condition like using potassium permanganate, alkaline or hot water bath, etc.) made the process less cost effective [31].

In the present paper, a simple cost effective method has been adopted for the synthesis of binary composites (i.e. MnO_2/PEDOT and MnO_2/PANI), where the unique morphology of MnO_2 has been explored for achieving high capacitance value. A nanocomposite material comprising of inorganic transition metal oxide like MnO_2 nanoparticle not only enhances the capacitance value due to synergistic effect, but also acts as a filler in polymer matrix of PEDOT or PANI and provides a stable structural configuration in the polymer matrix against its volumetric swelling and shrinking during processes of charge storage. To the best of our knowledge, the electrochemical performances of PEDOT–MnO_2 and PANI–MnO_2 nanocomposite as electrode material for symmetric supercapacitor cell with widened operating voltage window of 1.2 V using 1 M $LiClO_4$ in a non-aqueous electrolyte (acetonitrile) solution was investigated for the first time. Structural morphology and other characterizations were carried out using XRD, SEM, TEM, XPS and IR spectroscopy. The electrochemical performances of the supercapacitors were investigated by cyclic voltammetry (CV), galvanostatic charge/discharge cycling and electrochemical impedance spectroscopy (EIS) studies.

2. Experimental

2.1. Materials

3,4-Ethylenedioxythiophene (EDOT) monomer was obtained from BAYTRON Co. Aniline and poly-tetrafluoroethylene were obtained from Aldrich whereas acetylene black was obtained from Alpha Aesar. $MnSO_4$, $KMnO_4$, $FeCl_3{\cdot}6H_2O$, and n-hexane were the product of Merck. Sodium bis(2-ethylhexyl) sulphosuccinate (AOT) was purchased from Fluka.

2.1.1. Synthesis of nanorod MnO_2

α-MnO_2 in the form of nanorod were synthesized by redox reaction between stoichiometric quantities of $MnSO_4$ and $KMnO_4$ in aqueous medium. In a typical synthesis in aqueous medium, 10 mL of 0.1 M $KMnO_4$ solution was mixed with 10 mL of 0.15 M $MnSO_4$ solution and stirred continuously for 6 h. A dark-brown precipitate thus formed, was washed several times with distilled water, centrifuged, and then dried at 70 °C in vacuum drier for 12 h [32].

2.1.2. Synthesis of PEDOT–MnO_2 composite in n-hexane medium

A reverse microemulsion was first prepared by dissolving 19.12 mmol sodium bis(2-ethylhexyl) sulfosuccinate (AOT) in 70 ml of n-hexane. 10 mmol $FeCl_3$ in 1.0 ml distilled water was added to it and the mixture was gently stirred for 5 min. Previously distilled 3.52 mmol EDOT monomer was added to the reaction mixture followed by slow addition of 100 mg manganese dioxide nanoparticles (α-MnO_2) and kept for 3 h under gentle magnetic stirring. The blue-black precipitate of PEDOT–MnO_2 was filtered and washed with methanol followed by distilled water. Composite was dried under vacuum for 12 h at 80 °C. The loading of the α-MnO_2 nanoparticles in the composite sample is ~20%. Pure PEDOT polymer in n-hexane medium was also synthesized applying similar procedure in the absence of α-MnO_2 nanoparticles [33].

2.1.3. Synthesis of polyaniline–MnO_2 nanocomposite in aqueous medium

The PANI–MnO_2 nanocomposite was chemically synthesized by oxidative polymerization of aniline using $FeCl_3$ under controlled conditions. 100 mg α-MnO_2 was added to a mixture containing 0.1 M aniline in 100 ml of 0.5 M H_2SO_4 under stirring condition. Finally, 0.3 M $FeCl_3$ was added slowly to the reaction mixture at ice-cold condition. The greenish-black precipitate of the PANI–MnO_2 nanocomposite was filtered and washed with distilled water, methanol, acetone followed by diethyl ether for the elimination of the low molecular weight polymer and oligomers. Further, this precipitate was heated at 80 °C in a temperature-controlled vacuum oven. Pure PANI in aqueous medium was synthesized applying similar procedure in the absence of α-MnO_2 nanoparticles.

2.2. Sample characterization

Phase identification and morphological characterizations of α-MnO_2 and its composites were carried out using powdered X-ray diffractrometer (Philips PW 1710) with Cu Kα (λ = 1.5406 Å) radiation, transmission electron microscope (FEI model Tecnei G2 20S with 200 kV accelerating voltage and resolution of 0.2 nm) and scanning electron microscope (FEI model Quanta FEG 250). XPS core-level spectra were taken with an Omicron Multiprobe spectrometer (Omicron NanoTechnology GmbH.) fitted with an EA125 hemispherical analyzer. A monochromated Al Kα X-ray source operated at 150 W was used for XPS. The analyzer pass energy was kept fixed at 40 eV for all the scans. Infrared spectra for the identification of the characteristic bands were recorded using a PerkinElmer Spectrum 100 FTIR spectrophotometer employing transmission mode through KBr disc formation. The specific surface area of the samples were measured by nitrogen gas absorption through Brunauer–Emmett–Teller (BET) method, whereas the pore volume, average pore diameter and the pore size distribution were determined by Barrett–Joyner–Halenda (BJH) method using Quantachrome Autosorb surface analyzer.

2.3. Electrochemical measurements

Electrodes for supercapacitor were prepared using following procedure: 85 wt% electroactive materials (i.e. pure PEDOT, PANI and the composites) were mixed with 10 wt% acetylene black (AB) and 5 wt% polytetrafluoroethylene (PTFE) to form a thick paste. The paste was then pressed into a thin sheet of ~100 μm thickness using mortar and pastel. Finally, the sheet was compressed on a stainless steel mesh having the surface area around 1 cm^2. The prepared electrodes were dried at 60 °C for 6 h under vacuum. The total weight of the active material in the electrode is usually ~ 5 mg.

Electrochemical performances of the samples were observed using cyclic voltametry (CV) measurement (AUTOLAB-30 potentiostat/galvanostat). A platinum electrode and a saturated Ag/AgCl electrode were used as counter and reference electrodes respectively. All the CVs were measured between −0.6 and 0.6 V (i.e. operating window of 1.2 V) with respect to reference electrode at different scan rate (2–20 mV/s). Galvanostatic charge–discharge cycling and electrochemical impedance studies were performed with two-electrode system having identical electrodes made of same active electrode materials (i.e. Type-I symmetric supercapacitor). Constant current density ranging from 0.5 to 10 mA/cm^2 have been employed for charging/discharging the cell in the voltage range −0.6 to 0.6 V. The discharge capacitance (C) is estimated