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Design and synthesis of heteroatoms doped carbon/polyaniline hybrid material for high performance electrode in supercapacitor application

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ABSTRACT

Hybrid composites are very promising materials for the next generation high performance electrochemical supercapacitors. We have designed a hybrid composite electrode of heteroatom doped carbon with polyaniline (PANI) for supercapacitor. In order to dope heteroatoms in carbon, we have selected sulfonated PANI as a precursor and its carbonization resulted in N, S and O doped carbon (CNSO). CNSO-PANI hybrid composite has been synthesized by polymerizing aniline with CNSO via aqueous polymerization. Electrochemical performance of CNSO-PANI has been evaluated by cyclic voltammetry, charge-discharge cycling and electrochemical impedance techniques. CNSO-PANI has yielded a higher capacitance value of 372 F g^{-1} compared to pristine PANI (200 F g^{-1}) at 0.8 A g^{-1}, which indicates that the performance of PANI has been enhanced by the introduction of CNSO. This composite electrode has also exhibited excellent charge-discharge cycling stability, retaining over 78% of its initial capacitance after 6000 cycles with a coulombic efficiency of 99–100%, which is still 45% larger than the initial capacitance of pristine PANI. A phase angle value of 85° from the Bode plot has provided additional evidence of good capacitor behavior for the CNSO-PANI. The results demonstrate that PANI could be effectively utilized with the assistance of CNSO in supercapacitor.

1. Introduction

Supercapacitor or electrochemical capacitor is an energy storage device that uses to store and release energy [1]. Supercapacitors form a bridge between the batteries and the conventional capacitors by extracting the abilities of storing high energy and elevated power delivery. supercapacitors stand as longer cycle life, very fast rate of charge-discharge, outstanding cycle stability, low maintenance cost and find applications in hybrid electronic vehicles, space ship, portable electronics, fast acting short term power back up for UPS, laser pulsed, digital camera, etc., [2]. The energy storage mechanism in supercapacitors is based on mainly two types (i) the formation of electrical double layer by the separation of opposite charges at the electrode and electrolyte interface, typically known as an electrical double layer capacitor (EDLC), (ii) the faradaic charge transfer, typically called redox capacitor and the way of charge stored is dependent on the nature of the electrode components. Although traditional EDLCs comprise good cyclic stability, suffer from low energy density, which restricts their use alone in many fields, where high energy density is a key requirement. In pseudocapacitors, since the energy is stored by kinetic faradaic reactions via electron transfer, the energy density is higher by one order of magnitude in comparison with EDLCs; however, it suffers from the slow charge discharge rate. This leads to the increased attention of combining both the properties of EDLCs and the redox capacitors in a single hybrid material, trying to decrease or eliminate their drawbacks getting in an ideal way a synergic effect, which results in the development of new materials with new properties [3].

Carbon-based materials ranging from activated carbons to carbon nanotubes (CNTs) and graphene are the most widely used electrode materials for electrochemical supercapacitor applications [4–6]. Recently, carbon materials doped with heteroatoms, such as oxygen, nitrogen, phosphorus, and sulfur have attracted considerable attention for supercapacitor application due to the pseudo capacitance effect which is originated from electron donor/acceptor properties of heteroatoms [7–9]. In addition, the heteroatoms present in the carbon can improve the hydrophilicity of the carbon by the electrolyte [10]. As novel precursors for

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nitrogen-doping carbons, conducting polymers such as polyaniline (PANI) and polypyrrole (PPy) have gained much attention in recent years for their high nitrogen content [11–13].

Conducting polymers are generally attractive as they have a high charge density and low cost materials (compared with the relatively expensive metal oxides) [14]. Among the conductive polymers, PANI composites [15–21] have been extensively studied and well documented in the literature for supercapacitor applications, possibly due to high electrochemical activity, low cost, environmental stability and ease of syntheses.

In this work, thus we have made an attempt to develop supercapacitor by choosing the hybrid material based on carbon and polyaniline. In the present work, for the first time, we have used sulfonated polyaniline salt as a carbon precursor to prepare heteroatoms doped carbon (CNSO) and used for the synthesis of polyaniline composites (CNSO-PANI) via in-situ polymerization method, wherein the CNSO was added in different proportions during the polymerization of aniline. The spectral, morphological, thermal and electrochemical characteristics of the samples are discussed.

2. Experimental

2.1. Materials and instrumentation

Aniline, Chlorosulfonic acid ($ClSO_3H$), Dichloroethane (DCE) [S. D. Fine Chemicals, India], Ammonium persulfate (APS) and Sulfuric acid (H_2SO_4) [Rankem, India] were used as received. Freshly distilled aniline was employed in the reaction. All the reactions were carried out with distilled water and solvents.

XRD profiles for the powders were obtained on a Bruker AXS D8 advance X-ray diffractometer (Karlsruhe, Germany) with CuK_α radiation (land continuous) (λ=1.54 Å) at a scan speed of $0.045^\circ\,min^{-1}$. Powder samples were used by employing a standard sample holder. Morphology studies of the polymer powder samples were carried out with a Hitachi S-4300 SE/N field emission scanning electron microscope (FESEM) (Hitachi, Tokyo, Japan) operated at 20 kV. The polymer powder sample was sputtered on a carbon disc with the help of double-sided adhesive tape. Thermogravimetric analysis (TGA) was performed with TGA Q500 Universal (TA Instrument, UK) at a heating rate of $10\,^\circ C\,min^{-1}$ from ambient temperature to 700 °C under nitrogen atmosphere. The percentage of C, H, N and S in the samples were carried out by Vario Micro Cube Elementar, Germany. Specific surface area of the samples was determined by the Brunauer – Emmett – Teller (BET) method of nitrogen sorption at 77 K using a Quadrasorb-SI V 5.04 (Quantachrome Instruments corporation, USA). The samples were out-gassed at 200 °C for 6 h. before the measurement.

2.2. Preparation of electrode and electrochemical characterization

Working electrodes were prepared by pressing the polymer samples on stainless steel mesh (316 grade) with the application of $120\,kg\,cm^{-2}$ of pressure without any additional binder. Supercapacitor cell in the form of two-electrode Swagelok type without a reference electrode was constructed using two working electrodes (equal mass) separated by a cloth separator in 1 M H_2SO_4 electrolyte. Cyclic voltammetry and galvanostatic charge–discharge experiments were performed on supercapacitor cell with a WonATech multichannel potentiostat/galvanostat (WMPG1000, Gyeonggi-do, Korea). Coin cell (CR2032) was made using two electrodes separated by a non-woven polypropylene fabric separator and 1 M aqueous H_2SO_4 electrolyte. Electrodes for coin cell was made by pressing the mixture of 20 wt. % of graphite and 80 wt. % CNSO-PANI01 composite sample on stainless steel mesh with the application of $120\,kg\,cm^{-2}$ of pressure. Electrochemical impedance spectroscopy (EIS) measurement was performed with IM6ex (zahner-Elektrik, Germany) in the frequency range of 40 kHz to 10 mHz measured at an AC voltage amplitude of ±10 mV referring to equilibrium open circuit potential using three electrode cell configuration i.e., polymer electrode as a working electrode, platinum foil as a counter electrode and calomel electrode as a reference electrode. All electrochemical measurements were performed at ambient temperature.

2.3. Synthesis of heteroatoms doped carbon

Polyaniline-sulfate salt (PANI) was synthesized by oxidizing aniline using APS in 1 M H_2SO_4 by following our earlier report [22]. PANI was sulfonated using $ClSO_3H$. Solution containing 3.6 ml of $ClSO_3H$ in 50 ml of DCE was added to a solvent mixture containing 3 g of PANI in 150 ml DCE and refluxed at 80 °C for 4 h. The mixture was filtered, washed with cold water and acetone. Powder was dried at 50 °C in an oven. Both polyaniline-sulfate salt and sulfonated polyaniline salt were carbonized by heating up to 750 °C in a muffle furnace under nitrogen atmosphere for 30 min. In this work, carbonized polyaniline sulfate salt and sulfonated polyaniline salts are represented as CNO and CNSO.

2.4. Synthesis of polyaniline composites

Series of heteroatom doped carbon -polyaniline (CNSO-PANI) composites were prepared by aqueous polymerization of aniline using APS oxidant with the use of various amounts of CNSO. In a typical procedure, particular amount of CNSO was dispersed in 50 ml of 1 M H_2SO_4 solution containing 0.5 g of aniline. Oxidant solution was prepared by dissolving 1.14 g of APS in 50 ml of 1 M H_2SO_4 solution. The oxidant solution was added to CNSO-aniline mixture and the mixture was constantly stirred for 4 h. at ambient temperature. The reaction mixture was filtered under vacuum, washed with ample amount of distilled water and acetone until the filtrate is colorless. The obtained powder was kept in an oven at 50 °C for overnight. For comparison, polyaniline-sulfate salt was also prepared in the absence of CNSO. The ratios (w/w) of aniline to CNSO used were, 1:0.1, 1:0.2, 1:0.4, 1:0.6, 1:0.8 and 1:1 and the corresponding CNSO-PANI composites are labeled as CNSO-PANI01, CNSO-PANI02, CNSO-PANI04, CNSO-PANI06, CNSO-PANI08 and CNSO-PANI10 respectively.

CNO-PANI01 was prepared by following the above procedure with the use of 10 wt. % of CNO, instead of CNSO.

3. Results and discussion

The aim of this work is to improve the performance of the polyaniline electrode in supercapacitor with heteroatoms doped carbon. Heteroatoms doped carbon powder sample was prepared by the carbonization of polyaniline and sulfonated polyaniline salts. Sulfonated polyaniline salt (SPANI) was prepared by sulfonation of polyaniline. The elemental analysis of SPANI showed the presence of 6.9 wt. % sulfur. SPANI was dedoped to emeraldine base (SPANI-B), which showed the presence of 2.1 wt. % sulfur. The decrease of sulfur content from 6.9 to 2.1 wt. % is due to the removal of sulfuric acid dopant from SPANI during the dedoping process. The presence of sulfur in SPANI-B indicates that the sulfur is present on the aromatic ring of polyaniline in the form of–SO_3H group. The elemental analyses of carbonized polyaniline and sulfonated polyaniline salt showed the presence of nitrogen, sulfur and oxygen elements in carbon. The percentage of sulfur on carbonized polyaniline and sulfonated polyaniline salt was found to be 0.6 and 1.2 wt. % respectively. The presence of these heteroatoms can effectively enhance the surface activity and electrochemical performance of carbons due to the conjugation between the lone-pair electrons and the π-system of the carbon