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Nano-porous activated carbon from sugarcane waste for supercapacitor application

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ABSTRACT

Low cost with high specific capacitance and energy density is the critical and main requirement for practical supercapacitors. In the present work, nano porous activated carbon having specific surface area of 400 $m^2 g^{-1}$ from sugarcane waste (bagasse) has been synthesized and characterized as an electrode material for supercapacitor applications using ionic liquid based polymer gel electrolytes. The fabricated cell shows the overall specific capacitance of 372 mF cm^{-2} which is equivalent to single electrode specific capacitance of 248 F g^{-1}. The corresponding energy and power density of 16.3 Wh kg^{-1} and 1.66 kW kg^{-1} were achieved for EDLCs.

1. Introduction

Supercapacitors, also called as electrochemical capacitors or ultracapacitors are capable of providing large amount of energy in a short period of time, making them indispensable for fast power delivery [1–4]. In existing supercapacitors technologies most of the surface area resides in micropores that are not capable in forming electrical double layer; which results in the worst frequency response. Hence, energy stored in those carbon electrode materials can be withdrawn only at low frequencies. Nowadays, efforts have been focused on the development of supercapacitors having high energy and power density along with better frequency response for improved performance and more demanding applications [5–7].

Electrochemical double layer capacitors (EDLCs) have attracted a considerable attention due to their high power as well as energy density, excellent reversibility and long cycle life [8–9]. A wide range of carbonaceous materials like carbon aerogels [10], mesoporous carbons [11–12] and activated carbons [13–14], have been used as electrode materials in EDLCs.

Among these carbonaceous materials, biomass based activated carbon are most suitable because of its unique internal structure having regularly interconnected mesopores, high surface area, low mass density, notable chemical stability, acceptable electronic conductivity, low cost and environmental friendly nature makes it a promising electrode material for electrochemical double layer capacitors [2]. The large surface area of electrode is favorable for accumulating greater amount of charges leading to high energy density of the device. This ordered mesoporous structure enhances the diffusion rate of the charge carrier in the pore network which results in the better rate capability in high drain rate operations [15].

In the present manuscript, bagasse has been used as a biomass sample in order to prepare activated carbon. Chemical activation technique has been employed for the synthesis of bagasse based chemically treated activated charcoal (BCT) and has also been successfully checked as an electrode material for electrochemical double layer capacitor (EDLC) using ionic liquid as solid polymer electrolyte material. Ionic liquid based polymer gel electrolyte comprising of polyvinylidene fluoride hexafluoro propylene–1-ethyl-3-methylimidazolium bromide–propylene carbonate–Magnesium perchlorate, [PVdF(HFP)–(EMIM)(Br)–PC–$Mg(ClO_4)_2$] has been used because of its unique properties like low vapor pressure, high thermal stability and wide potential window [16]. The fabricated EDLC cell has been characterized by using a.c impedance, cyclic voltammetry and charge discharge techniques.

2. Experimental details

2.1. Preparation of ionic liquid based polymer electrolytes

The ionic liquid based polymer gel electrolytes using magnesium salts, [{polyvinylidene fluoride hexafluoro propylene}–{1-ethyl-3-methylimidazolium bromide}–{propylene carbonate}–{Magnesium perchlorate}] abbreviated as PVdF(HFP)–[EMIM]

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[Br]–PC–$Mg(ClO_4)_2$ has been prepared using standard "solution cast" techniques. In the process, initially the liquid electrolyte was optimized and prepared by dissolving 0.3 M magnesium salt in propylene carbonate (PC). The polymer PVdF-HFP and ionic liquid [EMIM][Br] was separately dissolved in acetonitrile. The liquid electrolyte was then mixed with the solution of PVdF-HFP/ [EMIM][Br]/acetonitrile in different weight ratios and stirred magnetically for 4–5 h. The concentration of PVdF-HFP and [EMIM][Br] was optimized and controlled at a ratio of 3:7. The viscous mixture was cast over glass petri dishes and acetonitrile was allowed to evaporate slowly, thereafter, free standing polymer gel electrolyte films (~400–450 μm) were obtained having ionic conductivity of $\sim 5.0 \times 10^{-3}$ S cm^{-1}. Finally the optimized polymer gel electrolyte of composition [PVdF(HFP) (30 wt%)–EMIM(Br) (70 wt%)] (30 wt%)–[PC–$Mg(ClO_4)_2$ (0.3 M)] (70 wt%) was used for the fabrication of supercapacitor cell.

2.2. Preparation of biomass charcoal and activated charcoal

Bagasse as a precursor material was obtained from the Guna district, Madhya Pradesh, India. Further it was cleaned from other materials such as sand or soil by washing it thoroughly. After that it was sun dried for 2–3 days. The dried bagasse was then kept in muffle furnace at 300 °C for 5 h. The charcoal was then soaked in chemical solution $CaCl_2$ (25 wt%) for 18–20 h and thereafter it was washed with double distilled water and kept in oven at 110 °C (overnight) for drying. Finally, chemical activation using KOH as an activating agent has been used for the synthesis of activated charcoal. The details of the procedure have been given elsewhere [17].

2.3. Construction of electrodes used in the experiments

The electrodes were prepared by making slurry of prepared activated charcoal powder and PVdF-HFP in the ratio 90:10 (w/w) in a common solvent acetone by thorough mixing. Fine films of electrodes were coated by spraying the slurry on carbon cloth (Ballard, USA) and kept in oven at 70 °C for 10–12 h by spraying the slurry on carbon cloth (Ballard, USA) and kept in oven at 70 °C for 10–12 h. The geometric surface area of electrode was taken as 1.0 cm^2 having 3.0 mg cm^{-2} as the mass of active electrode material.

2.4. Instrumental details

The pore texture characteristics and pore size distribution of the prepared activated charcoal was measured volumetrically with a Micrometrics Instruments, Gemini Model 2380 surface analyzer by N_2 desorption–adsorption technique using liquid N_2 at 77 K. The specific surface area was determined by using Brunauer–Emmett–Teller (BET) method in the pressure range (P/P_0) between 0.05 and 1.0. The pore size distribution (PSD) studies were carried out by using Barrett–Joyner–Halenda (BJH) method which was applied in the desorption branch of the isotherm. The sample was degassed at 300 °C for 2 h prior to adsorption experiments. X-ray diffraction studies have also been carried out by using D8 Advance, Bruker AXS Company, Germany using an operational voltage of 40 kV and current of 40 mA respectively by using CuKα radiation. A SEM-EDX image of the synthesized sample has been obtained by using FESEM, Zeiss, Ultra Plus 55. Thermogravimetric analysis (TGA) of the sample was performed after preheating it at 100 °C to remove adsorbed moisture and residual solvent. Then the mass loss was monitored in a thermogravimetric analyzer (TGA EXSTAR 6300).

2.5. Electrochemical measurements

Electrochemical measurements of the fabricated supercapacitor cells were carried out in a two-electrode cell. The cell has been fabricated as per the following configuration:

Cell A: BCT | [PVdF(HFP)−(EMIM)(Br)–PC–$Mg(ClO_4)_2$] | BCT

where BCT: bagasse based chemically treated activated charcoal and [PVdF(HFP)–(EMIM)(Br)–PC–$Mg(ClO_4)_2$] is optimized composition of polymer gel electrolyte used in the present studies and can be described as [{polyvinylidene fluoride hexafluoro propylene}–{1-ethyl-3-methylimidazolium bromide}–{propylene carbonate}–{magnesium perchlorate}].

The performance characteristics of the EDLC cell was carried out by using cyclic voltammetry, galvanostatic charge–discharge studies and a.c impedance spectroscopy with the help of computer controlled CHI 608C, CH Instruments, USA.

3. Results and discussion

3.1. Characterization of activated carbon

Activated carbons are high surface area and porous materials that are synthesized either by thermal or chemical activation method. It consists of small hexagonal rings called as graphene sheet. The size orientation and stacking of these sheets are determined by their synthesis method. During its activation process, the thermal energy involved is sufficient enough to break the links between adjacent graphene sheets which allows some of them to orient themselves in parallel. Fig. 1 shows the typical XRD pattern of BCT that consists of graphitic-like microcrystallites which are randomly oriented and distributed throughout the sample and confirms its turbostratic structure [18–20]. It can be clearly seen from the figure that there exists two broad diffraction peaks at 25° and 41.6° corresponding to (0 0 2) and (1 0 0) structural phases respectively which confirms the formation of activated charcoal.

In order to visualize the microstructure of the activated carbon, scanning electron microscopy (SEM) was performed and is shown in Fig. 2(a). Since the minor metallic impurities are generally associated with biomass based activated carbon therefore BCT has also been analyzed with energy dispersive X-ray spectroscopy (EDX) along with SEM and are shown in Fig. 2(b). EDX spectra reveal that the biomass based activated carbon contains minor quantities of silicon and oxygen. The presence of these elements is possibly due to the nature and history of biomass sample used (bagasse). The SEM image of BCT clearly shows the irregular and porous texture throughout the carbon surface, which facilitates the proper switching in and out of ions within the available pores and are mainly responsible for the better electrochemical performance of the devices.

Nitrogen adsorption–desorption isotherms of bagasse based activated carbon at 77 K are shown in Fig. 3. The isotherm is of type IV according to the IUPAC nomenclature [21] and it confirms the

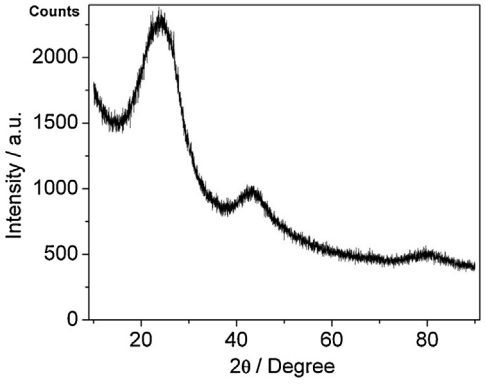

Fig. 1. XRD pattern of bagasse based activated charcoal.