Journal of Power Sources 262 (2014) 224–231

Contents lists available at ScienceDirect

Journal of Power Sources

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

Activated carbon made from cow dung as electrode material for electrochemical double layer capacitor

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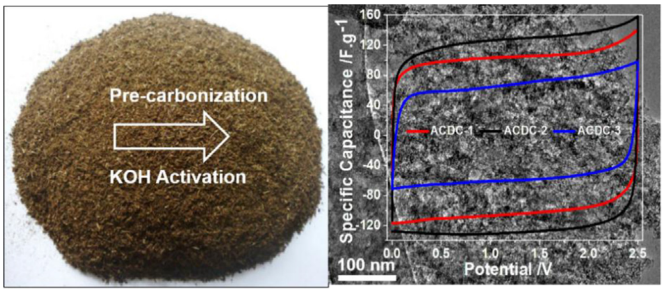
HIGHLIGHTS

- Cow dung is used as a carbon precursor, which is an abundant biological waste.
- Synthesized activated carbon has high surface area with suitable amount of mesopore.
- Inherently present inorganic and organic materials leads to high amount of pores.
- High specific capacitance along with excellent durability is achieved.
- Capacitive performance has significant dependence on mesopore–micropore ratio.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 February 2014
Received in revised form
29 March 2014
Accepted 30 March 2014
Available online 4 April 2014

Keywords:
Cow dung
Activation
Supercapacitor
Organic electrolyte
Two-electrode system

ABSTRACT

Cow dung is one of the most abundant wastes generated on earth and has been traditionally used as fertilizer and fuel in most of the developing countries. In this study activated carbon is synthesized from cow dung by a modified chemical activation method, where partially carbonized cow dung is treated with KOH in different ratio. The synthesized activated carbon possesses irregular surface morphology with high surface area in the range of 1500–2000 m^2 g^{-1} with proper amount of micropore and mesopore volume. In particular, we demonstrate that the surface morphology and porosity parameters change with increase in KOH ratio. These activated carbons are tested as electrode material in two-electrode symmetric supercapacitor system in non-aqueous electrolyte and found to exhibit high specific capacitance with excellent retention of it at high current density and for long term operation. In particular, the activated carbon synthesized at 2:1 ratio of KOH and the pre-carbonized char shows the best performance with specific capacitance of 124 F g^{-1} at 0.1 A g^{-1} and retains up to 117 F g^{-1} at 1.0 A g^{-1} current density. The performance is attributed to high surface area along with optimum amount of micropore and mesopore volume.

1. Introduction

Carbon materials are used in wide range of applications depending on their electrical conductivity, polarizability, chemical inertness and structural strength along with tuneable electrical, thermal and optical properties [1–3]. Amongst them, porous carbon materials are very popular as electrode materials for Li secondary battery, supercapacitor, dye sensitized solar cell, and fuel cell [4–11]. Porous carbon materials have been synthesized by various methods such as hard or soft sacrificial template by using silica or surfactant, catalytic activation by using metal salts or

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http://dx.doi.org/10.1016/j.jpowsour.2014.03.143

organometallic compounds, carbonization of polymer blends and aerogel, chemical activation, physical activation, and etc [6–12]. Owing to consumption of expensive precursor, energy as well as time, development of simple low-cost strategies is still a foremost challenge for synthesis of nanostructured carbon materials [12]. Natural biomass-based organic materials, which are present ubiquitously on earth, therefore have emerged as a plausible alternative for carbon precursor. Several biomass-based materials such as rice straw, gelatin, pine needles, coffee bean, corn stalk, cow dung etc are employed to synthesize nanostructured carbon materials with high surface area and tuneable porosity [13–22]. In developing world, cow dung has been used for centuries as cooking fuel, sanitizing cleanser, construction material, insulation, and waterproofing for walls and floors in rural houses, cultural symbol in religious worship, and raw-material for producing organic composite and generating electricity. Despite of being a cheap and abundant source for synthesizing functional carbon materials, cow dung has not been explored much. Among the few reports that can be found in literature, Demiral et al. [17] have reported the synthesis of activated carbon with high surface area from cow dung using $ZnCl_2$ and KOH activation. On the other hand, Das et al. [23] have utilized activated carbon synthesized from cow dung for removal of Cr(IV) ions from water. But, to the best of our knowledge after extensive literature survey, cow dung carbon has been unexplored in any electrochemical application.

Supercapacitor, alias electrochemical capacitor is a promising candidate for high energy storage due to its outstanding advantages such as high power density (10^3–10^4 W kg^{-1}), long cycle life ($>10^6$ cycles), pulse power supply, low maintenance cost, simplicity and better safety compared to secondary batteries [1,24–27]. Electric vehicles can be considered as a platform for use of supercapacitor when high power density is needed during acceleration and the energy can be recovered during braking. Depending on mechanism of charge storage, supercapacitors can be categorized in two major classes, i.e. electrochemical double-layer capacitor (EDLC) and pseudocapacitor. The capacitance of EDLC comes from non-faradic charge accumulation at interfacial double layer of electrode and electrolyte, whereas in pseudocapacitors, reversible faradic redox reactions also add up the capacitance along with non-faradic charge [24–27]. Carbon materials with high surface areas are generally used as EDLC electrodes, while conducting polymers and metal oxides are used in construction of pseudocapacitors [26–28]. Although specific capacitance of pseudocapacitors are often better than EDLC, slow rate and probable irreversibility of faradic processes lead to degradation of performance of pseudocapacitors at higher current density and also in long term operation [25–27]. Specific surface area, pore structure of electrodes, ionic conductivity and voltage stability of electrolyte are the main factors which regulate the energy stored in EDLC [29]. High specific capacitance can be achieved in aqueous electrolyte due to their high conductivity, small ionic size and probable faradic process, but it is unfavourable to use aqueous electrolytes due to possible corrosion of current collector and smaller electrochemical window. Organic electrolytes have high potential window and also, are non-corrosive. Therefore, organic electrolytes are often utilized for getting high energy density and durability in EDLC application.

Microporous activated carbon materials are found to be usual choice as electrode materials, which deliver high capacitance and power density due to their very high surface area and pore volume as well as low cost [27–32]. Contrary to a common perception that specific capacitance is directly related to specific surface area, ultramicropores (pore size $\leq$ 0.8 nm) in activated carbons are non-accessible to big organic electrolyte ions, and eventually the active electrode/electrolyte interface area is only partially realized in such system, producing lower specific capacitance than expected [33,34]. Therefore it is necessary to have sufficient mesopore volume and their good interconnectivity for organic electrolyte to effectively reach all the available surface area in carbon framework [35–38]. Thus, an appropriate control over mesopore/micropore volume and proper choice of electrolyte is expected to be crucial to ensure a good performance of supercapacitor in terms of both power delivery rate and energy storage capacity. Alkali activation is the most effective method for synthesis of porous carbon, for which, NaOH or KOH is used most commonly and mainly results in microporous carbon materials [14,39–45]. Usually, the synthesis of activated carbons by alkali activation approach includes two steps: pyrolysis of precursors at a moderate or high temperature under inert atmosphere to obtain a carbon-enriched char, followed by high temperature pyrolysis of the char mixed with alkali to create a porous structure [46].

In this study, we have synthesized activated carbon from a cheap and abundant biological waste i.e. cow dung by using KOH as activating agent. The as-synthesized activated cow dung carbon (**ACDC**) has high amount of mesopores along with micropores formed by KOH. The inorganic materials inherently present in cow-dung is found to be responsible for formation of mesopores. As a result of optimum combination of mesopore/micropore, the **ACDC** exhibits excellent performance as electrode material for supercapacitor.

2. Experimental section

2.1. Synthesis

The activated cow dung carbon (**ACDC**) was synthesized by chemical activation method using KOH as an activating agent and pre-carbonized cow dung char as a precursor. Initially, the sun-dried cow dung was pre-carbonized at 450 °C for 2 h under constant N_2 flow. Then, the char was mixed with KOH in different proportions in minimum volume of water and stirred at 80 °C until formation of homogenous slurry. The slurry was then transferred to an alumina crucible and pyrolyzed under constant N_2 flow at 800 °C with temperature ramp rate of 10 °C min^{-1} and then maintained there for 2 h before natural cooling. The obtained product was washed with 1.0 M HF to remove inorganic impurity and then with deionized water till the filtrate became neutral. The products were finally dried overnight at 80 °C. The amount of KOH to char ratio in terms of weight was varied from 1 to 3 and thus obtained carbon was designated as **ACDC-1**, **ACDC-2** and **ACDC-3**.

2.2. Surface characterization of various carbon materials

The surface morphologies of the synthesized **ACDC**s were characterized by field emission scanning electron microscopy (FE-SEM) using a Hitachi S-4700 microscope operated at an acceleration voltage of 10 kV. N_2 adsorption-desorption isotherms were measured at −196 °C on Micromeritics ASAP 2020 surface area and porosity analyzer after the carbon sample was degassed at 150 °C to 20 mTorr for 12 h. The specific surface area (S_{BET}) was determined from nitrogen adsorption in the relative pressure range from 0.05 to 0.2 using the Brunauer–Emmett–Teller (BET) equation. The total pore volume (V_{total}), micropore volume (V_{micro}) and pore size distribution were determined by density functional theory (DFT) method. Electrical resistivity of the **ACDC** samples was measured by four probe method at different pressures using a custom-made cell described in earlier work [47]. X-ray diffraction (XRD) patterns of samples were obtained using a Rigaku Smartlab diffractometer with CuKα radiation using a Ni β-filter at a scan rate of 2°/min. The X-ray source was operated at 40 kV and 30 mA.