Electrochimica Acta 240 (2017) 43–52

Contents lists available at ScienceDirect

Electrochimica Acta

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

Research Paper

Hierarchical porous carbon from hazardous waste oily sludge for all-solid-state flexible supercapacitor

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ARTICLE INFO

Article history:
Received 11 February 2017
Received in revised form 22 March 2017
Accepted 13 April 2017
Available online 14 April 2017

Keyword:
Oily sludge
Hierarchical porous carbon
Supercapacitor
Cost-less electrode material

ABSTRACT

Rationally packed porous carbon with high ion-accessible surface area and low ion-transport resistance is proved to be an excellent candidate as electrode materials in high performance supercapacitors. However, its cost-effective fabrication still remains a significant challenge. Here, we report on a novel three-dimensional hierarchical porous carbon (HPC) synthesized via a facile and low-cost approach from hazardous waste oily sludge for the first time. Both the smart "self-template" effect and appropriate activation effect are crucial for the rational hierarchical porous structure. The "self-template" procedure is the key point for creating the skeleton of carbon, and the KOH activation process is able to regulate pore size distribution and increase specific surface area. The as-fabricated HPC possesses favorable features for supercapacitor, such as outstanding specific surface area (2561 $m^2 g^{-1}$), large pore volume (2.25 $cm^3 g^{-1}$), tunable and large range of pore size distribution. The HPC-based electrode can deliver an admirable capacitance of 348.1 $F g^{-1}$ at 0.5 $A g^{-1}$ and 94.3% capacitance retention at 5 $A g^{-1}$ after 10,000 cycles in aqueous electrolyte. Remarkably, the all-solid-state HPC//HPC symmetric supercapacitor displays outstanding capacitance of 81.3 $F g^{-1}$ at 0.5 $A g^{-1}$ with high energy density of 7.22 W h kg^{-1}. It is demonstrated that the strategy developed here would provide cost-effective production of HPC electrode material for high performance supercapacitors and offer a promising avenue of large-scale fabrication of HPC from other hazardous industrial waste.

1. Introduction

Nowadays, the challenge of searching high-efficiency and environment-friendly energy sources to solve the problem of environment pollution and decreasing availability of fossils fuels becomes increasingly considerable [1]. Supercapacitors, as one of the most promising energy storage, have drawn great attentions thanks to their excellent characteristics of high specific power, good cyclic stability, and fast charging processes. And currently, these high parameters promote the replacement of traditional batteries in many electrical systems, such as consumer electronics, motor electrical systems, memory back-up systems, and industrial power and energy management [2].

The energy storage properties of supercapacitors are mainly determined by the electrode materials [3]. As is well known, carbon materials play the dominant role in commercial supercapacitors since their high porosity and electrical conductivity [4]. Up to now, some significant achievements have been made in fabrication of carbon materials with outstanding nanostructures for electrode. In the aspects of preparation techniques, a variety of methods including hard/soft templating [5,6], hydrothermal synthesis [7], chemical vapor deposition [8], arc discharge and laser ablation [9] have been reported. Although some of them have emerged as promising techniques, an economically viable method for the preparation of macroscopic quantity of carbon nanostructured materials under reasonable experimental conditions is still lacking to date. On the other hand, carbon materials with high degree of porosity and high specific surface area such as activated carbons [10], templated porous carbons [11], carbon nanotubes (CNTs) [12], carbon nanofibers [13], graphene [14] and its derivatives [15–18] were successfully synthesized. However, the prohibitive prices are still hindering their practical applications, due to expensive equipment or raw materials and tedious fabrication processes. For example, the current market price are 140 \$ g^{-1} for multiwall carbon nanotubes (95%, research grade) [19], 200 \$ g^{-1} for single wall carbon nanotubes (95%, CVD) [20],

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http://dx.doi.org/10.1016/j.electacta.2017.04.061
0013-4686/

200 $ g^{-1} for graphene (98%) [20], and 130 $ g^{-1} for graphene oxide (99%) [20]. Therefore, synthesis of cost-effective carbon materials with delicate structures in facile way has become a research hotspot in recent years.

Recycling of waste products for synthesis of carbon materials has been considered as a promising solution for cost cutting recently [21]. With the rapid development of modern industry, more and more environment polluting wastes were produced. As a carbon precursor, the reuse of some organic waste including agriculture wastes [22], food [23], municipal sludge [24], and even dung [25], has attracted tremendous attention because of their various potential applications, such as carbon dioxide capture, hydrogen storage, catalyst support, and electrodes for batteries and supercapacitors.

Oily sludge is a common waste in the petroleum industry during crude oil exploration, production, transportation, storage and refining processes [26]. It mainly contains water, petroleum hydrocarbons and other recalcitrant components, which seriously threaten to the environment. And even worse, more than 60 million tons of oily sludge can be produced each year and more than 1 billion tons of oily sludge has been accumulated worldwide [27]. Due to their hazardous nature and increasing volume around the world, appropriate managements have become a worldwide problem. Considering the huge amount and abundance of hydrocarbons content in oily sludge, it is feasible to convert it into high value-added carbonaceous materials for application in supercapacitors. This strategy could meet the urgent demand for both oily sludge disposal and costless carbon materials. However, the high ash content in oily sludge still remains a challenge for advanced utilization.

Here, we report on a facile route to design and fabricate hierarchically porous carbon (HPC) by using oily sludge as precursor. The as-synthesized HPC exhibits favorable features for supercapacitor, such as high specific surface area, tunable pore size distributions and exceptionally chemical mechanical robustness. More importantly, such HPC material cost nearly free. To the best of our knowledge, it is the first time to realize oily sludge-based carbon electrode materials for supercapacitors. Such unique HPC exhibits a high gravimetric specific capacitance (348.1 F g^{-1} at 0.5 A g^{-1}) and excellent cycling capability (94.3% retention at 5 A g^{-1} after 10,000 cycles). When used as electrodes for supercapacitor, an all-solid-state symmetric flexible device with excellent rate capability (71.2% retention at 20 A g^{-1}) and high energy density (7.22 W h kg^{-1}) can be achieved.

2. Experiment section

2.1. Material

The oily sludge was collected from tank bottom of Dongying storage depot of petroleum, Sinopec. Before processing, the oily sludge was dried at 80 °C overnight. All the Chemical reagents were of analytical grade and used as received without further purification.

2.2. Preparation of HPC

In a typical process, 10 g of oily sludge (OS) was ground into particles in an agate mortar and carbonized in a tube furnace at 700 °C for 2 h under nitrogen (99.9%) flow of 50 mL/min. The resulting oily sludge-based carbon (OSC) was immersed in 100 mL of 1 M HF, and then evaporated at 100 °C in the fume hood. The obtained solid product was washed with distilled water until the pH reached to 7 and then dried at 105 °C for 6 h to generate de-ashed carbon (OSDC). Subsequently, the as-obtained OSDC was impregnated in 1 M KOH solution with KOH/C ratios of 3:1, and then dried at 80 °C. Activation process was carried out at 700 °C for 2 h in a fixed-bed reactor under slow N_2 flow (50 mL/min), with the heating rate of 10 °C/min. When the system cooled down to room temperature under N_2 atmosphere, the received product was washed with 1 M HCl solution and then plenty of distilled water. After drying in oven at 105 °C for 6 h, the HPC-3 was obtained. For comparison, the as-obtained OSDC was impregnated in different volume 1 M KOH solution with KOH/C ratio of 2:1 and 4:1, respectively. Other procedures were the same as those used to fabricate HPC-3. The resulting products ware designated as HPC-2, HPC-4, respectively.

2.3. Structure characterization

The proximate analysis of OS samples was conducted according to ASTM D3173-03, ASTM D3174-04 and ASTM D3175-02 standards. The results were expressed in terms of moisture, ash, and volatile matter. The element analysis was performed on Vario ELIII elemental analyzer. XRD patterns were recorded from Philips X'Pert Pro Super diffractometer with Cu Kα radiation (λ=1.54178 Å). The field emission scanning electron microscopy (SEM) images were carried out on a JEOL JSM-6700F SEM. The transmission electron microscopy (TEM) images were obtained on a JEOL-2010 transmission electron microscope at an acceleration voltage of 200 kV. Multipoint N_2 adsorption-desorption experiment was performed on an automatic Micromeritics ASAP 2020 analyzer at 77 K. The sample was outgassed at 200 °C for 6 h in vacuum before adsorption measurement. The specific surface area was calculated by BET method and the pore size distribution plots were generated from desorption branch of the isotherm by the Non-Local Density Functional Theory (NLDFT) methods. Raman spectroscopy was performed using LabRAM HR800 microscopic confocal Raman spectrometer at a laser wavelength of 514 nm. X-ray photoelectron spectra (XPS) of the samples were detected by an ESCALAB MK II with Mg Kα (hυ= 1253.6 eV) as the excitation source. All binding energies obtained in the XPS spectral analysis were corrected for specimen charging by referencing C1 s to 284.8 eV arising from adventitious hydrocarbon.

2.4. Electrochemical evaluation

All electrochemical characterizations were carried out on a CHI660E electrochemical workstation at room temperature. The test was firstly performed by using a three-electrode system in 6 M KOH aqueous electrolyte solution. A Pt foil and Hg/HgO electrode acted as counter and reference electrode, respectively. To prepare the working electrode, 80 wt % as-prepared carbon materials (HPC), 10 wt % carbon black, and 10 wt % polyvinylidene-fluoride (PVDF) were mixed in N-methyl-2-pyrrolidone (NMP) to form homogeneous slurry. Then the resulting slurry was coated on a nickel foam (current collector) as a 1 cm × 1 cm sheet, followed by drying at 80 °C overnight. The mass of active materials loaded on the working electrode was about 4.0 mg/cm^2. Cyclic voltammetry (CV) curves were obtained in the potential range of −1.0–0 V vs. Hg/HgO by varying the scan rate from 5 to 100 mV s^{-1}. Charge/discharge measurements were performed galvanostatically (GCD) at 0.5–50 A g^{-1} over a voltage range of −1.0–0 V vs. Hg/HgO. Electrochemical impedance spectroscopy (EIS) was measured in a frequency range of 100 kHz to 0.01 Hz at open circuit voltage.

2.5. Fabrication of the all-solid-state supercapacitors

Two symmetric working electrodes were prepared by the same procedures as aforementioned. To prepare alkaline solid electrolyte, 1.12 g KOH (20 mmol) and 2.0 g polyvinyl alcohol (PVA) were added into 20.0 mL distilled water. Then, the whole mixture was